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Nutrients recovery and recycling in algae processing for biofuels production

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ABSTRACT

The supply of nutrients is a great issue to a sustainable scale-up of microalgal biofuels production, as these photosynthetic microorganisms require large amounts of N, P and other micronutrients to grow, which turns into high fertilizers demand. Additionally, recovery and reuse of nutrients (particularly N & P) are a must to reduce the non-point pollution emanating from their release into water or air during the downstream processing steps to biofuels or bioproducts. In the recent years, strong research efforts have been paid for developing nutrient recovery and recycling techniques, in order to reduce the net amount of fertilizers required. One possibility is exploiting nutrients from waste streams, such as wastewaters, while others focus on the recovery of N and P from the non-fuel fraction of the produced microalgal biomass, which is then recycled to the cultivation system, in a closed-loop perspective. In both cases, the presence of possible contaminants as well as nutrients bioavailability can impact the biomass productivity compared to standard synthetic media. Although the nutrients recovery and reuse has been in the forefront for a few years, there are no review publications available yet. In this paper, state-of-the art studies on nutrients recovery and recycling methods in microalgae processing from the last decade are reviewed. The study focuses on the different N and P recovery methods and yields, as well as on their subsequent use in algal cultivation and impact on algae productivity. Possible bioproducts exploitation is considered, and perspectives of closed-loop material balances on a large-scale are eventually provided.

1. Introduction

Microalgae are photosynthetic organisms able to produce numerous valuable compounds, such as fatty acids, proteins, pigments, and polysaccharides. Among all these, algal biomass is identified as a promising feedstock for the production of renewable liquid fuels and bioproducts thanks to its high growth rate, biochemical composition, and oil content compared to conventional energy crops [1,2].

Microalgae cultivation stands out over terrestrial crops mainly because they do not require arable land hence not directly competing with food production. Despite these acknowledged advantages, first process assessments often neglected the nutrients requirement to achieve significant biomass and biofuels productions on a large scale. In fact, microalgal biomass contains about three times the amount of nutrients compared to terrestrial plants [3], so that competition between energy (i.e. fuels), bio-products, and food production might actually be shifted from land to fertilizers issues.

Only in the last decade the problem of nutrients demand in industrial microalgae cultivation became a matter of concern in the scientific community, with special concern to nitrogen and phosphorus [3]. Inorganic nitrogen compounds are produced via the Haber-Bosch process, which involves H_2 derived from fossil sources as a reactant, together with high temperature and pressure, resulting in elevated process energy duties, and CO_2 emissions [4]. Phosphorus, on the other hand, is derived from phosphate mines, already largely exploited for agricultural crops. Recent studies showed that current rates of mined phosphorus utilization for food production are not sustainable, and phosphate reserves are expected to be depleted in the next 50–100 years [4–6].

Based on the elemental composition of microalgal biomass, and assuming 100% uptake, it is estimated that roughly 40–90 kg of N and 3–15 kg of P are required to produce 1 t of algae [6–8]. Simple material balances and resources assessments allow understanding that, if significant displacement of petroleum-derived fuels is to be achieved, these amounts cannot be sustainably met by fertilizers supply. For example, the production of 19 billion liters per year of algal oil-based fuels (roughly 25% of the target established by the United States Energy Independence and Security Act for 2022), would require 41–56% and 32–49% of N and P_2O_5 fertilizers world surplus, respectively [6]. This would likely affect fertilizers market prices, further lowering the economics of algal biofuels production. Moreover, considering that research on renewable fuels is driven by the need of reducing carbon

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dioxide emissions in the atmosphere, such a high fertilizers consumption might be counterproductive in this regard, due to the release of CO_2 in their production process [9].

Therefore it is quite clear that N and P need to be recovered from alternative sources, e.g. by exploiting wastewaters or by recycling process streams. In particular, since the oil fraction of microalgae contains only little amounts of these elements, N and P could be recovered from the biomass and recycled for further production, reducing the net fertilizers input. In the past decade, and especially in the second half of it, intense research has been focused on the investigation of possible techniques to achieve this goal.

This review paper aims at providing a comprehensive analysis and comparison of nutrients (mainly N and P) recovery and recycling methods developed in microalgae processing so far, as well as at understanding how the different recycled media affect the biomass productivity. Perspectives of material balances for large-scale applications are eventually discussed.

2. Nutrients requirement in algal cultivation

Microalgae require specific amounts of essential macro- and micronutrients to grow. Carbon, nitrogen and phosphorus are the important macronutrients, [10], which need to be supplied to the culture in bioavailable forms for an efficient uptake. Concerning C, microalgae as photosynthetic microorganisms mostly uptake the inorganic form of CO_2, dissolved in the medium. Several studies [11–13] have successfully evaluated the possibility of supplying inorganic C also in the form of soluble bicarbonate, exploiting the equilibrium of carbon ions in solution [3]. In addition, some microalgae are able to uptake organic molecules (e.g., glucose, acetate, glycerol), as a source of both carbon and energy. However, even though mixotrophic cultivation usually results in higher growth rates, the cost of organic substrates makes it an impracticable choice for large-scale biofuels production. Although C supply is certainly of great importance in microalgae cultivation, it is not the focus point of this review.

Nitrogen, which is essential for amino acids and proteins synthesis, is commonly taken up in the inorganic forms of NO_3^- or NH_4^+ [3]. The latter one, which is the inorganic N form prevailing in most waste streams, is potentially the preferred source by microalgae as, being the most reduced form, it requires less energy to be assimilated. Nonetheless, care must be paid when supplying ammonium to the cultivation medium, as in solution it is in chemical equilibrium with free ammonia, which is toxic on microalgae cells above a concentration of about 2 mM [3,14]. This drawback can indeed be controlled by either regulating the pH and/or using proper concentrations. In addition to inorganic forms, some microalgal species are able to assimilate organic nitrogen molecules. Among the most common ones is urea, but a few strains are also reported to be capable of up-taking simple amino acids [15,16].

Phosphorus, on the other hand, is mainly taken up by microalgal cells from the medium in the form of orthophosphates, while other inorganic or organic forms of P generally require to be first mineralized and converted to orthophosphates in order to be assimilated [3].

Besides C, N and P, microalgae require the presence of several other trace nutrients in the cultivation medium, such as K, Mg, S (as SO_4^{2-}), Ca and Fe, among others. Despite the small quantities required, these micronutrients are essential components of the biomass.

Standard cultivation media are formulated so that all the necessary nutrients are present in adequate amounts and ratios (see Table 1), ensuring no limitation to growth. These formulations are usually based on the Redfield ratio for phytoplankton, which considers C.N:P proportions of 106:16:1 on molar basis [17]. However, evidence has shown that microalgae composition can diverge from this ratio, and it can adapt to the environmental composition, according to nutrient availability [18]. For example some microalgae, when cultivated in a phosphorus-rich medium, tend to accumulate the excess P as intracellular polyphosphate reserves, for later use in case the medium becomes P-depleted. This phenomenon is known as luxury uptake [19], and should be avoided to maximize P utilization. In addition to the medium composition, nutrients uptake also depends on cultivation conditions, such as light intensity and, in continuous cultures, dilution rate (i.e., specific growth rate) [20,21]. As a result, the uptake of nutrients in microalgal cultivation is indeed a complex phenomenon, so that the actual amounts required to achieve high productivities are even greater than those predicted by most life cycle assessment (LCA) analyses, which consider 100% uptake efficiencies [4,7,22,23]. Therefore, it appears even more important to develop nutrients recycling technologies.

3. Seawater and wastewaters as nutrient sources

The use of alternative water sources in place of freshwater for large-scale algal cultivation has been largely encouraged. This would be beneficial both in terms of water footprint (the life-cycle usage of freshwater would be greatly reduced [8]) as well as of macro and micronutrients supply. Fig. 1 shows different nutrients-rich sources that could be exploited for algal cultivation.

Seawater contains excess amounts of most of the micronutrients required for algal growth, especially potassium, but also magnesium and sulfur. In addition, little amounts of nitrogen and phosphorus, as well as CO_2 absorbed from the atmosphere, are dissolved in the marine water environment [8,24,29,30]. Clearly, the use of seawater is limited to marine microalgae (such as *Nannochloropsis* sp. *Tetraselmis* sp.), even though a medium containing 10% of seawater has been proposed for inexpensive cultivation on freshwater algae and cyanobacteria [31]. In any case, the concentration of N and P in saline water is not sufficient to sustain significant algal growth, so it must be increased by a suitable technique in order to achieve substantial biomass productivities.

Wastewaters, on the other hand, are generally rich in N and P. In fact, the possibility of growing algae in wastewaters has gained a lot of interest because of the double advantage of simultaneously treating polluted effluents and producing valuable biomass [3]. Depending on the source, wastewaters have different compositions and characteristics, which determine their suitability for microalgae cultivation and the resulting productivity, as detailed here below.

3.1. Municipal wastewaters

Urban wastewaters have been widely investigated as viable nutrients sources for microalgae growth [26,32–34]. Although nutrient concentrations in municipal wastewaters depend on the stage of the depuration process (primary or secondary treatment), microalgae have been shown to efficiently uptake N (mainly present as NH_4^+, with little amounts of NO_3^- and NO_2^-) and P from this source, both in batch and in continuous cultivation [25,35]. Remarkable values of specific growth rates (about 0.7 d^{-1} and 1 d^{-1}) are reported for *Chlorella protothecoides* [32] and *Scenedesmus obliquus* [25], respectively. However, the final biomass production is limited by the relatively low nutrients concentrations: for N it typically ranges between 20 and 40 $mg\,L^{-1}$, for P between 3 and 10 $mg\,L^{-1}$ [4,6,9,25,32], values that would allow reaching biomass concentrations not more than 0.5 $g\,L^{-1}$. Other studies exploited the effluents coming from the anaerobic digestion of either municipal wastewater [36] or of the activated sludge produced from municipal wastewater treatment [37], to efficiently cultivate the marine alga *Nannochloropsis*. These streams are more concentrated compared to the starting wastewaters, so that higher biomass concentrations can be reached, even though proper dilutions are needed to avoid inhibition. Regardless the treatment process stream considered, the amount of all municipal wastewaters available could only give a small contribution (1–5%) to the total N and P requirements necessary to satisfy the current transportation fuels demand of a large city [4,6,9].