



## Hydroxyapatite and dittmarite precipitation from algae hydrolysate

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### ABSTRACT

Several research efforts across the globe have been concerned with addressing the technical barriers in the commercialization of algae-based sustainable biorefineries. Nutrients cost and management and in particular, phosphorus, have been highlighted as one of the most significant challenges in algae cultivation and downstream processing. In this study, 83 wt% of phosphorus present in *Scenedesmus* sp. microalgae was extracted as water-soluble phosphate in aqueous phase via flash hydrolysis process while preserving the algae lipids. Subsequently, the phosphate containing aqueous phase (algae hydrolysate) was used for producing dittmarite and hydroxyapatite by two different mineralization processes. In the first pathway, more than 97 wt% of the phosphate in the hydrolysate was recovered in the form of carbonate-hydroxyapatite, a valuable biomaterial, at 280 °C within one hour of residence time via hydrothermal mineralization process. Whitlockite as the secondary phase was also observed along with the hydroxyapatite. In the second pathway, 67 wt% of the phosphate and 6 wt% of nitrogen were recovered as dittmarite (magnesium ammonium phosphate), an effective slow-release fertilizer, at 20 °C via an atmospheric precipitation process. The effects of seeding, temperature, reaction time, and mineralizers to PO<sub>4</sub> molar ratio on phosphate removal as well as product yield were studied. This is the first kind of study in which flash hydrolysis and mineralization processes were integrated to provide an energy efficient platform for phosphorus recovery from microalgae in forms of value added compounds that could be suitable for long-term storage and handling. Through this experimental study, we report the shortest residence time for hydroxyapatite precipitation from an algal hydrolysate. The short residence could substantially save in reactor size and processing time as well as provide an option for high throughput which could result in a significant cost reduction in algae to bioproducts and biofuels.

### 1. Introduction

Microalgae are as an attractive feedstock for biofuels and bioproducts due to its lipids, proteins, and carbohydrates content as well as its adaptable growth conditions [1]. A variety of pathway and process developments have been investigated in order to accelerate the commercialization of algal-based biorefineries [2,3]. In spite of improvements in algal productivity and development on different downstream processing routes, the barriers for large-scale commercialization have not yet been removed [2]. Algae biomass and biofuels production costs are dependent on the nutrients use; particularly nitrogen and phosphorus [1]. Phosphorus is of greater concern in large-scale algae cultivation due to its irreplaceability and the fact that it is obtained from a non-renewable phosphate rocks through mining [4,5]. Recent collaborative studies supported by the U.S. Department of Energy and the National Academies Press outlined nutrients supply and recycling as a critical hurdle for a sustainable algae-to-fuel process [3,6]. Multiple studies have been dedicated to nutrients recycling and management

either separately or in conjunction with the biofuel production processes, such as direct recycling of the aqueous phase produced by the hydrothermal liquefaction (HTL) of microalgae [7–9] or the aqueous phase (hydrolysate) obtained from the flash hydrolysis (FH) [10–12] process. Although, the results from these studies have shown the feasibility of direct nutrients recycling approach, it possesses several practical challenges. One of the main challenges is the fact that all of these nutrients are dissolved in the aqueous phase; therefore, any type of handling, shipping or storage needs to account for the huge amount of water associated with these nutrients [8,10,11]. The need for dilution of the aqueous phase to reduce the concentration of growth inhibitors (e.g. phenolic compounds) [11] in addition to N:P ratio adjustment are other challenges involved in this approach. Further, organic content and nutrients present in the aqueous phase is a rich medium for bacterial growth resulting in decomposition of the nutrients such as organic nitrogen [11]. All of these obstacles and limitations eliminate the potential for long-term storage. To address these challenges, the current study provides a novel method of on-site nutrients

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recovery from microalgae in the forms of two value-added products (hydroxyapatite and dittmarite) which can be stored and used for various applications.

In the proposed approach, nutrients are extracted in algae hydrolysate using flash hydrolysis (FH) process [10–16]. FH is a continuous subcritical water extraction process which has been shown to extract phosphorus (> 80 wt%), nitrogen (> 60 wt%) and inorganic elements (S, K, Na, Ca, Mg, Cl, etc.) in aqueous phase (algae hydrolysate) in only 10 s of residence time, while preserving lipids in a solid biofuels intermediate. These solids recovered after FH of microalgae have the same fatty acid profiles as the original biomass [12,13,15]. Applying this method to the wet algal biomass offers an environmentally-benign technique to extract phosphates in the hydrolysate while enhancing the quality of the biofuels intermediates for biofuels/bioproductions downstream processing.

Conversely, mineralization is a technique to precipitate specific elements from an aqueous medium such as algae hydrolysate. Conceptually, it is driven from the earth-mimetic mineral precipitation (deposits) phenomena. In other words, imitating the natural mechanism of the earth to form insoluble minerals at appropriate conditions [17,18]. This process could be either at hydrothermal conditions (hydrothermal mineralization, HTM) or atmospheric pressure (atmospheric precipitation, AP) based on the desired target products (e.g. hydroxyapatite (HAp) or dittmarite). The HTM technique has been applied for resource recovery (B, F, P, As, Sb, Cr, and Nd) and polluted water detoxification in the last decade [18–26].

In this study, the extracted *Scenedesmus* sp. microalgae nutrients (phosphorus and nitrogen) via FH process, were recovered through two different precipitation/mineralization pathways (Fig. 1) to produce HAp and dittmarite by the addition of calcium (Ca) and magnesium (Mg) as mineralizers via the HTM and AP processes, respectively. Ca and Mg are essential micronutrients in algal cultivation due to their vital role in microalgae cell wall structure and chlorophyll molecule [27]. Therefore, these are partly available in the algal hydrolysate. The addition of extra mineralizer (Ca or Mg sources) helps in meeting the stoichiometric ratio to precipitate HAp and dittmarite compounds.

HAp ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is the most thermodynamically stable calcium phosphate mineral at pH between 4 and 12 at normal temperatures [28,29]. Its broad range of applications include synthetic bone, implant filling and coating, chromatography, corrosion resistant materials, drug delivery as well as catalytic activity [30–38]. HAp production has been conducted under a variety of physical and chemical conditions [39]. However, most studies have been performed on mixtures of pure model compounds rather than applied to the actual phosphate and calcium rich aqueous streams [39]. Dittmarite, on the other hand, is the monohydrate form of magnesium ammonium phosphate (MAP –  $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ ) salt. The hexahydrate form is known as struvite; however, in this study dittmarite and MAP may use interchangeably. MAP precipitate where phosphate and ammonium-rich streams are introduced to alkaline conditions. Its application includes swine wastewaters [40,41], urine waste [42], beverage wastewater [43], landfill leachate [44], poultry manure [45], industrial wastewater [46], anaerobic digester effluents [47,48], and synthetic wastewater [49]. This white crystalline compound is considered a promising slow-release fertilizer for crops [50] and recently as a nutrients source for algal cultivation [16,51,52].

Phosphate recovery in the form of HAp and dittmarite from the complex ionic/cationic algal hydrolysate with high organic content has

never been studied before. The proposed integrated FH-HTM/AP processes can be robust methods that have the potential to be applied in algae processing for on-site nutrients and biofuels intermediate recovery. Due to better heat integration, this will improve the energy utilization during process stages, resulting in final product price reduction. Unlike a recent study by Griffin et al., the HAp precipitated from the algae hydrolysate using FH-HTM pathway conducted at a relatively lower temperature (280 °C compare to 350 °C), the product was not mixed with any other type of solid compounds. Not to mention that particular method was only applicable for a special microalgal species that has been cultivated in a calcium-rich medium [53]. A related point to consider is the one-hour hydrothermal reaction in the current study is in contrast to couple of hours/days [54–56] of residence time.

The objectives of this study are to (1) investigate the feasibility of HAp and MAP precipitation from the phosphate-rich algal hydrolysate through integrated FH-HTM and FH-AP processes, (2) evaluate the effect of seed inoculation on the nutrients removal and precipitates' property and structure in both pathways, (3) determine the effect of temperature, Mg/PO<sub>4</sub> molar ratio, and the reaction time on the phosphate removal in the FH-AP process, (4) characterize all solid and liquid phases in each step including the original *Scenedesmus* sp. microalgae, hydrolysate from FH, phosphate-depleted aqueous phase (after HTM/AP reactions), in addition to the recovered precipitates, (5) assess the structure, morphology, and crystallinity of the precipitates.

## 2. Materials and methods

### 2.1. Microalgae strain and characterization

*Scenedesmus* sp. microalgae which was cultivated in the biomass research laboratory (BRL) at Old Dominion University using the modified BG-11 in the photobioreactors, was used for this study. Upon harvesting, algae biomass was freeze dried and stored in an airtight container at a temperature below –20 °C until use. Elemental and proximate analyses in addition to the inorganic elemental composition were performed to fully characterize the algal biomass. Thermo Finnigan Flash EA 1112 elemental analyser (ThermoFisher Scientific, Waltham, MA) was used to determine the C, H, and N content of the freeze dried microalgae. 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) standard (certified number 202147–10/03/2015, ThermoFisher Scientific, Cambridge, UK) was used as a standard. Approximately, 1 mg of solid sample was placed in a 5 × 9 mm tin capsule (CE Elantech, Inc., Lakewood, NJ) for combustion in a furnace at 950 °C. The oven temperature was at 65 °C and the flow of the helium carrier gas was 100 mL/min. Each experiment was conducted in triplicate and the reported values are the average (± standard deviations). Inorganic elemental composition was measured using X-ray fluorescence (XRF) spectroscopy (Bruker S4 Pioneer, Bruker Corp., Billerica, MA). In order to determine proximate analysis (including ash, moisture, volatile, fixed carbon), thermogravimetric analyser (TGA) (TGA-50H, Shimadzu Corporation) was used and the method has been explained elsewhere [53]. Major elements (C, N, and P) of the initial biomass have been tracked in every stage along the process. Lipid content of the microalgae and the biofuels intermediates were measured gravimetrically, using the Bligh-Dyer method. Soxhlet extraction was carried out for 24 h with 2:1 (v/v) chloroform:methanol solvent, followed by drying and weighing the extracted lipids [57]. Phosphate analysis was conducted using concentrated nitric acid-sulfuric acid

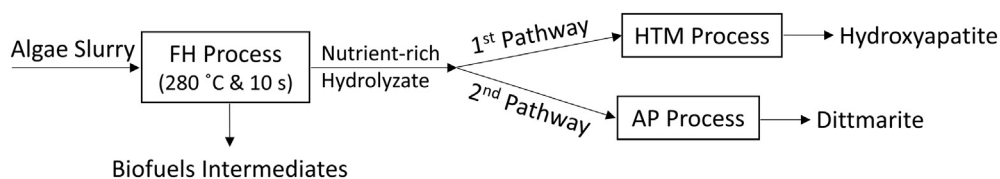


Fig. 1. Schematic diagram of the proposed integrated pathways for nutrients recovery. FH: flash hydrolysis, HTM: hydrothermal mineralization, AP: atmospheric precipitation.

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