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Contamination levels in biomass and spent media from algal cultivation system contaminated with heavy metals

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ABSTRACT

Sustainability assessments have shown that integrating CO_2 from power plants with microalgae production systems can reduce costs and greenhouse gas emissions. However, coal fired flue gases contain contaminants (heavy metals) that could have a deleterious effect on products derived from such systems. To address this concern, photobioreactors (PBRs) were designed to test the hypothesis that metals in a microalgae cultivation system at concentrations derived from flue gas will limit end uses of the biomass and spent medium. *Scenedesmus obliquus* were grown in PBRs spiked with 10 metals found in such flue gases at concentrations representing typical (1X) and high (5X and 10X) metal loading scenarios. Results show that contamination levels can be modulated by managing the harvesting time and by leaching, with EDTA being effective at early growth stage (approximately ≤ day 6) and acidified methanol effective afterwards. Although metals limit biomass and medium uses, some uses fall within regulatory limits (e.g., 1X spent medium is suitable for irrigation, and 1X biomass is suitable for bio-fertilizer and select animal feed uses). Results showed that uses of biomass and medium under higher loading scenarios from such integration will restrict end uses of both biomass and media.

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1. Introduction

In response to increased global energy consumption and concerns over the effects of greenhouse gases, several new regulations for reducing carbon emission from industrial point sources are being implemented in several countries. One of the carbon trapping technologies being explored is the integration of photosynthetic organisms such as microalgae with point source carbon dioxide (CO_2) emissions [1]. Microalgae utilize solar energy 10 times more efficiently than terrestrial plants resulting in high biomass and lipid yields [2]; but they require a concentrated carbon source such as industrial flue gas, with the integration of the two systems being mutually beneficial. However, the utilization of flue gas from various fuels including coal may concurrently introduce contaminants [3,4] (such as the heavy metals listed in Table B1 in the SI) into the growth system as shown by previous studies [5,6]. Previous research shows that cell density, biodiesel yields, and metal distribution are affected when microalgae is grown in a multi-metal system at concentration level estimated to come from flue gas with most metals accumulating in the biomass [7].

Techno-economic evaluations of large-scale microalgae production systems often assume a seamless integration of the cultivation system with a low cost CO_2 source such as flue gas producing industries. These studies assume that spent medium can be re-used and the biomass harvested from such systems can be used for animal feed, human food source, bioenergy feedstock, etc. [8–13], without considering any metal contamination. However, the buildup of contaminants within the biomass and spent medium has the potential to limit the end use of microalgae based products and byproducts due to adverse effects of heavy metals on human/animal health and the environment [1]. Depending on the level of heavy metal contamination, the biomass and the medium may not be adequate for the uses proposed in such techno-economic evaluations, or may need to be treated prior to their use or release to the environment.

The information about the extent of heavy metal contamination in the biomass and medium for a microalgae system using flue gas is limited in the current literature. Wide variability in the initial metal concentration and the metals loading rates is expected for a cultivation system using flue gas. This variability originates from several intrinsically variable factors such as: the variable metal concentration in the fuel supply, which varies across coal types and regions [14]; the variable removal efficiency of air pollution control devices (APCD) [15]; the variable trace elements in the water used (e.g. seawater, agricultural runoff, recycled algal spent media, municipal and industrial wastewater); among others. To address this complexity, this study takes a conservative approach by maximizing the contact time through the use of a batch cultivation system (instead of a fed batch approach) and by

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evaluating three scenarios (named 1X, 5X and 10X) intended to capture the wide range of possible intermediate concentrations in the complex metal loading scenarios that could occur in a field cultivation system where recycling of the medium is expected. Primary assumptions for determining the baseline concentration are based on the integration of microalgae cultivation systems with coal based flue gas (see detailed assumptions and calculation in [7]). Higher heavy metal exposure doses of 5X and 10X were 5 times and 10 times the 1X concentration, respectively.

Thus, this study addresses the hypothesis that heavy metals present in a microalgae cultivation system will limit potential end uses of products, co-products and by-products. The key objectives of this study are: 1) to determine the metal concentration in the biomass and medium that corresponds to three metals loading scenarios expected to be introduced from coal-based flue gas, 2) to identify management practices (harvesting time, growth dilution and leaching) as means to modulate the contamination levels in biomass, and 3) to identify potential uses and limitations for the contaminated algal biomass and medium based on current regulatory standards. This study aims to provide the algae research community with preliminary feasibility information about how different levels of heavy metals could affect algae-based products and how some strategies (such as harvesting time, growth dilution and the use of a leachant) can help with the compliance and planning of potential uses. Moreover, the authors recognize the complexity of this issue and from the beginning attempted to design a research program that addresses the stated hypothesis while providing a path forward for a more comprehensive research program to support the development of microalgal biofuels and bioproducts.

2. Materials and methods

Microalgae were cultivated in vertical tube photobioreactors (PBRs) (Fig. A1 in SI) over a 24 day period under various heavy metal concentrations (1X, 5X, and 10X) with the baseline concentration (1X) intended to be a conservative estimate of contamination levels from the integration of a growth system with coal flue gas (calculations detailed in [7]). Increasing concentrations (5X, 10X) were used to understand impacts of higher metal loading scenarios. Over the course of the growth period, heavy metals were quantified in the biomass and medium, and the results were used to evaluate the limitations of the use of the biomass and spent medium. The effectiveness of solvents typically used in various industries was evaluated for metal removal.

2.1. Growth system

The nutritive medium used was composed of $NaNO_3$ (1000 mg L^{-1}), K_2HPO_4 (200 mg L^{-1}), $MgSO_4 \cdot 7H_2O$ (49.1 mg L^{-1}), $CaCl_2 \cdot 2H_2O$ (25.1 mg L^{-1}), $MgCl_2 \cdot 6H_2O$ (21.5 mg L^{-1}), H_3BO_3 (11.4 mg L^{-1}), $MnCl_2 \cdot 4H_2O$ (0.597 mg L^{-1}), $ZnSO_4 \cdot 7H_2O$ (0.086 mg L^{-1}), $Na_2MoO_4 \cdot 2H_2O$ (0.058 mg L^{-1}), $CuCl_2 \cdot 2H_2O$ (0.041 mg L^{-1}) and $CoCl_2 \cdot 6H_2O$ (0.029 mg L^{-1}). This mixture was autoclaved at 121 °C. To avoid iron precipitation with medium components during autoclaving, $FeSO_4 \cdot 7H_2O$ and $Na_2EDTA \cdot 2H_2O$ solution were separately autoclaved and were added to the medium prior to inoculation to reach concentrations of $Na_2EDTA \cdot 2H_2O$ (12 mg L^{-1}) and $FeSO_4 \cdot 7H_2O$ (4.5 mg L^{-1}) in the final medium. The initial pH was adjusted to 7.0 by HCl addition. *Scenedesmus obliquus*, donated by Arizona Public Service (APS), was chosen for this study because of its ability to thrive well in high CO_2 concentrations [16–18] and due to APS's experience with this algal strain. APS developed test bed experiments and evaluated them using microalgae to sequester CO_2 from the flue gases from power plants with different fuel source: Cholla plant is coal fired and Red Hawk uses natural gas. *S. obliquus* thrived in both situations.

For the experiment *S. obliquus* was grown axenically in petri dishes in order to maintain strain purity. Colonies of microalgae from petri dishes were harvested and grown in 3 L polystyrene spinning bioreactors (Corning®) with nutritive medium for 7 days until cultures reached a density of approximately 2.5 g L^{-1} (dry weight basis). Light was supplied by cool fluorescent lamps (24/7) and pH was maintained at 7.0 by CO_2 injection. Biomass was harvested by centrifugation (3900 RPM for 5 min) and washed twice with fresh medium in order to eliminate metal chelators excreted by microalgae (adapted from Bates et al. [19]). Prior to microalgae cultivation, the PBRs were acid rinsed overnight using 10% HNO_3 and then were rinsed thoroughly with deionized water. The PBRs were autoclaved at 120 °C for 30 min and filled with sterile medium without EDTA in order to reduce complexation with metals.

Heavy metals were prepared as individual liquid stocks at 1000X concentrations. The stocks were sterilized by filtration through sterile 0.2 μm sterile syringe filter (instead of autoclaving) in order to avoid changes in the oxidation state. The day of seeding, sterile medium was added to the bioreactor. Air delivery system was turned on, followed by adding heavy metals to the bioreactors with concentrations 1X, 5X or 10X, with 1X composed of As (0.078 mg L^{-1}), Cd (0.015 mg L^{-1}), Co (0.016 mg L^{-1}), Cr (0.13 mg L^{-1}), Cu (0.131 mg L^{-1}), Hg (0.01 mg L^{-1}), Pb (0.054 mg L^{-1}), Ni (0.25 mg L^{-1}), Se (0.01 mg L^{-1}) and Zn (0.44 mg L^{-1}). The growth system was operated in batch mode and allowed the determination of contamination levels of microalgae under the longest time of exposure and the highest initial metal concentration expected; therefore giving insights of maximum contamination levels. A real flue gas fed system is expected to have variable initial metal concentration ranges depending on coal source and a variable exposure time to metals, resulting from the incremental flue gas feeding rates directly proportional to cell multiplication. As a consequence, potentially variable intracellular uptake (driver of metabolic-induced toxicity) could be expected, thus impacting the final contamination levels in biomass and spent medium.

Washed algal biomass was added to each PBR to reach a final density of 0.8 g L^{-1}. The final volume of 1.1 L was achieved by dropwise addition of medium. The mixing of the algal cells in the PBR and the maintenance of pH at 7.0 was accomplished by sparging the PBR with CO_2 enriched air through a vertical glass capillary tube that extended down to 1 cm from the bottom of the PBR. CO_2 delivery was monitored daily and adjusted to maintain the pH at 7. Biomass content was determined as total suspended solids (TSS) through dry mass and optical density measurements.

2.2. Heavy metals sampling

Two analytical methods were used to determine metal concentrations. The first method was used to detect As, Cd, Co, Cr, Cu, Ni, Pb, Se and Zn. A total of 12 mL of unfiltered sample (algal suspension) was aspirated from a PBR of which 5 mL was used for analyzing the heavy metal concentration in the algal suspension. The remaining 7 mL was centrifuged at 7500 RPM for 3 min and the supernatant was analyzed for heavy metal concentration and is reported as heavy metal concentration in the medium. The wet biomass pellet was then evaluated for desorption of heavy metals by EDTA and is reported as the EDTA non-removable fraction as described below. The total metals in the harvested biomass were determined through the difference between the total metals in the aspired unfiltered sample and the metals in the supernatant. Unfiltered samples, supernatant samples and microalgae pellet samples were transferred into borosilicate test tubes and digested with HNO_3 at 105 °C in a heating block until biomass was no longer visible. Digested samples were transferred into volumetric flasks with the volume adjusted to 5 mL (1X experiments) or 10 mL (5X and 10X experiments) using deionized water type I. Samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICPMS Agilent 7500 Series). ICPMS metal standards and quality control (QC) samples were prepared as detailed in Napan et al. [20] the night before or the same day of the analysis using concentrated analytical grade stocks (ICPMS 6020, High Purity Standards, USA) [20].

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