



Implementation of UV-based advanced oxidation processes in algal medium recycling

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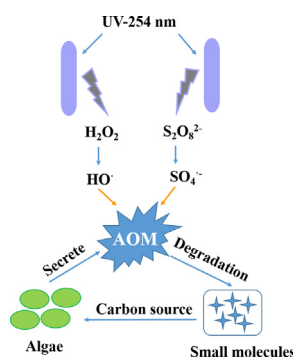
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HIGHLIGHTS

- Degradation of AOM by advanced oxidation processes were reported.
- UV/PDS and UV/H₂O₂ process could convert the growth inhibitors into nutrient.
- AOPs-treated media promoted algal growth in the recycled culture.
- The economic comparison of UV/PDS and UV/H₂O₂ were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Algae show great potential as sustainable feedstock for numerous bioproducts. However, large volume of water consumption during algal biomass production makes that the culture media recycling is a necessity due to economic and environmental concern. To avoid the negative effect of enriched organic matters in the harvested culture media, pre-treatment prior to medium replenishment and reuse is required. In this study, degradation of algal organic matters (AOM) in the culture media by UV-based photolysis processes (i.e., direct UV, UV/peroxydisulfate (PDS), UV/H₂O₂, and UV/NH₂Cl) was explored. The results showed that UV, UV/PDS, UV/H₂O₂ and UV/NH₂Cl caused a decrease of SUVA for 29.9%, 35.4%, 40.45%, and 22.6%, respectively, though the organic matter was almost not mineralized. Fluorescence excitation-emission matrix combined with parallel factor analysis indicated that UV/PDS and UV/H₂O₂ degraded 47.26%–56.31% of the fulvic-like and humic-like fractions in AOM. Powder activated carbon adsorption and growth evaluation for the AOPs-treated media indicated that UV/PDS and UV/H₂O₂ processes not only could remove the growth inhibitors in the media, but were also beneficial to the algae growth. These results suggested that UV/PDS and UV/H₂O₂ could effectively degrade the hydrophobic components in AOM and converted the growth inhibition fraction of AOM in the recycled media into nutrient source for algal growth. Different from the general application of UV-based AOP in the wastewater

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treatment, this study provided an innovative idea about how to pre-treat AOM in the media recycling: utilization rather than removal, which was a more sustainable and environment-friendly technology.

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1. Introduction

There is increasing recognition of the importance of algae in recent years because of its huge potential as sustainable feedstock for food and feed products, materials, chemicals, fuels and various high-value products (Ruiz et al., 2016), the mitigation of greenhouse gases released into the atmosphere (Shirvani et al., 2011), and application in the wastewater treatment (Zhou et al., 2013). However, the use of algal biomass as a feedstock for bioproducts is limited because of the substantial amount of water usage in the algal cultivation. It was reported that 997 kg of water is required to produce 1.0 kg of microalgal biomass (Richardson et al., 2014). Recycling of the medium not only reduces water costs and the cost of nutrients that are still present in the medium in substantial amounts after harvesting, but also reduces the potential environmental impacts associated with disposing of the very large volumes of water used in algal culture (Borowitzka and Vonshak, 2017). Therefore, recycling of the medium after harvesting is essential for economic and environmental sustainable biomass production.

Recycling of culture media is not always successful. As early as 1940, Pratt and Fong reported that *Chlorella* cells could produce and liberate a growth-inhibiting substance into the external solution (Pratt et al., 1944). It is recognized that organic metabolites are naturally excreted by algae during the growth or suddenly released when cell lysis occur (McGrattan et al., 1976). Furthermore, nutrient limitation, which is used as measure to enhance lipids production, is a stress factor enhancing metabolites excretion (Hu et al., 2008). These algalogenic organic matters (AOM) that excrete into culture medium could cause growth inhibition, algal aggregation and affect the content of lipid in the recycling cultivation. Thus, to remove the negative effect of AOM becomes a prerequisite to feasibly utilize recycled culture media.

Pretreatment technologies for recycled media attracted much attention in recent years. For example, (Morochó-Jácome et al., 2015) found granular activated carbon absorption could reduce 73.7% organic matter and 52.4% pigment in the recycled media of *Arthrospira platensis*, and combining with ferric chloride coagulation, the total removal rate for organic matters and pigment could reach 92.3% and 95.3%, respectively (Morochó-Jácome et al., 2016). (Fret et al., 2016) studied the combined effect of pH induced-flocculation and sand filtration for the removal of particles in the recycled media of *Nannochloropsis* sp., and found the total removal rate reached 78%. Nevertheless, in the practical utilization, the absorbents need to replace or regenerate frequently, which is a costly and time-consuming work. Advanced oxidation processes (AOPs) are attractive and promising technology to destruct organic pollutants by highly oxidizing agents (Zhang et al., 2015). UV-based AOPs, which are based on the generation of reactive radicals, such as hydroxyl radical ($\cdot\text{HO}$), sulfate radical ($\text{SO}_4\cdot^-$) or amino radical (Wu et al., 2012), have been studied as efficient and environmentally friendly treatment technologies to destruct organic pollutants (Xu et al., 2016). UV/ H_2O_2 , UV/PDS and UV/ NH_2Cl have been successfully applied in the wastewater and drink water treatment (Sun et al., 2016). To date, few studies have investigated the removal of AOM by AOPs.

The objective of this study was to evaluate the efficiency of UV/ H_2O_2 , UV/PDS and UV/ NH_2Cl processes in pretreatment of harvested algal culture media for reuse. The treated culture was replenished with nutrient and inoculated with algae to test its growth-supporting effect. The chemical and energy costs during the UV-based AOPs were also determined. We intended to find an economic and environmental sustainable method with easy scale-up to pre-treat the recycled media. To our best knowledge, this study is among the first to investigate the degradation of AOM in recycled media by UV-based AOPs.

2. Material and methods

2.1. Algae cultivation and culture media collection

The strain *Scenedesmus acuminatus* GT-2 was obtained from the Freshwater Algae Culture Collection of the Center for Microalgal Biotechnology and Biofuels, Institute of Hydrobiology, Chinese Academy of Sciences. *S. acuminatus* GT-2 was cultured in 15 L indoor panels with modified BG11 media with specific conditions (Table 1). The light paths for the panel reactors were 5 cm. Air with 3% (V/V) CO_2 was bubbled into the reactors. The cultures were harvested using an ultrafiltration (UF) membrane with a molecular weight cut-off (MWCO) of 50 kDa (Zhang et al., 2010). The permeate was used for the following AOPs.

2.2. Apparatus and procedure of AOPs

Experimental Setup and condition were similar with Sun et al. and Zhang et al. (Sun et al., 2016; Zhang et al., 2015). Briefly, four types of AOPs were conducted in a 100 mL magnetically stirred cylindrical quartz reactor with a UV lamp (power is 40 W, rated voltage is 220 V, wave-length is 253.7 nm, Philips, Netherlands). The UV radiation time of UV process was 100 min while the time of UV/ H_2O_2 , UV/PDS and UV/ NH_2Cl processes was 30 min. The original harvested culture media was used as a control.

2.3. Absorption with powder activate carbon

We compared the absorption capacity of powder activated carbon (PAC, 100 mesh, Sigma-Aldrich, USA) and granular activated carbon (12–40 mesh, Norit, Netherlands), and coconut shell activated carbon (CSAC, 3–5 mesh, Norit, Netherlands) and found PAC showed higher removal efficiency to AOM (Supplementary Fig. S2). Therefore, PAC was selected in the sequential absorption experiments. The dose-response curve and adsorption kinetic curve were conducted (Supplementary Fig. S3), and it was found that PAC with a dose of 20 g/L and absorption time for 30 min showed the highest removal to AOM in the original culture media. This absorption condition (PAC, 20 g/L, 30 min) was used to maximize the absorption of AOM in the original and AOP-treated culture media. All the activated carbons were washed with deionized (DI) water (conductivity = 18.2 $\text{M}\Omega \cdot \text{cm}$, Milipore, USA) until the TOC of effluent water was lower than 0.5 mg/L.

2.4. Analysis

The bulk concentrations of the total organic matters in the filtered culture media samples before and after AOPs treatments were measured using a TOC-L Series analyzer (Shimadzu, Kyoto, Japan). The UV_{254} was measured using HACH DR600 Spectrophotometer (HACH, Loveland, Colorado, USA) in the quartz cuvette of 1 cm, and DI water

Table 1
Growth conditions of *Scenedesmus acuminatus* in the 15 L panel PBR.

Species	<i>Scenedesmus acuminatus</i>
Experiment duration	12 days
Initial inoculum	Exponential phase, 0.1 g/L dry weight
Media type	BG11 (with 0.1875 g/L NaNO_3)
Temperature	26–28 °C
pH	6.5–7.0
Light intensity	220 $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, continuously supplied
Bubbling air+ CO_2	6 L/min air with 2%–5% CO_2

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