ADSORBENT-BASED ALGAL CULTIVATION SYSTEM TO FACILITATE INTEGRATION OF ALGAL BIOFUEL PRODUCTION WITH WASTEWATER TREATMENT

BY

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DISSERTATION

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ABSTRACT

Although combining algae cultivation with wastewater treatment has been highlighted as a promising pathway for sustainable biofuels, there are still several challenges that limit the ability to use algae for biological wastewater treatment. First, the treatment performance of an algal wastewater system is less stable than current systems using aerobic heterotrophic bacteria. For instance, Garcia et al. (2005) showed significantly increased effluent ammonia concentrations during the nighttime. Secondly, the turbidity of wastewater limits the penetration of light into the system, which reduces photosynthesic efficiency. Third, previously reported algae cultivation systems require up to 10 times more land area because of longer hydraulic retention times (HRTs) and shallow tankage designed to maximize solar energy capture.

To address the challenges listed above, this study reports on the development of a novel adsorbent-based algae cultivation system that improves the efficiency and reliability of integrated systems that provide both wastewater treatment and sustainable algal biomass production at a reasonable cost. Chapter 3 investigated the benefits of integrating adsorbents into an algal wastewater treatment system and found that adding granular activated carbon (GAC) and/or zeolite was able to improve both the effluent water quality and biomass productivity.

In Chapter 4, a commercially available rotating algal biofilm system (Algaewheel®) was used to evaluate the technical barriers of using algae to treat swine wastewater and subsequently convert the wet mixed biomass to biocrude oil via hydrothermal liquefaction (HTL). Three different hydraulic retention times (HRT) were used to study the effects of nutrient loading on the removal of nutrients and biocrude oil yield. The results were used to develop an advantageous operational strategy aimed at maximizing algal biofuel yield combined with relatively high nutrient removal efficiency.

In Chapter 5, the long-term benefits of integrating adsorbents into algal wastewater treatment systems were investigated. The adsorbent amended system was able to recover faster from shock loading events and provided more stable effluent quality. Moreover, this research demonstrated for the first time that algae wastewater treatment systems can be successfully operated with continuous recycling of HTL aqueous product (PHWW). The system without adsorbents had a significant reduction of biomass productivity when the PHWW concentration in

the influent was above 1.5%. In contrast, the system with adsorbents had increased biomass productivity when PHWW added. The effects of service time on the adsorbents were also investigated. After 10 months of usage, activated carbon capacity was reduced by 40%, but the adsorption rate was not significantly different than virgin activated carbon. In contrast, after 10 months usage, zeolite had only a slight reduction in adsorption capacity, but the adsorption rate was reduced by an order of magnitude. These results indicated activated carbon might need to be regenerated after longer term usage (years) and zeolite may need some occasional washing operations to control the surface biofilm thickness and restore adsorption kinetics.

Chapter 6 conducted a techno-economic analysis for three different scenarios of algal wastewater treatment system coupled with biofuel production and nutrient recycling methods. The results showed that an adsorbent integrated Algaewheel® system coupled with HTL and recycling PHWW had the lowest biofuel production cost ($10.7/gal). In comparison,other alternative scenarios with Algaewheel/HTL/Catalytic Hydrothermal Gasification (CHG) and High rate pond/Extraction/Anaerobic digestion had biofuel production costs of $11.7/gal and $13.2/gal, respectively. Wastewater treatment credits and electricity credits were then estimated and included to calculate the minimum fuel selling price. The results showed wastewater treatment credits could potentially cover all the costs for biofuel production. Sensitivity analysis suggested that the HRT of the system and the biocrude oil yield had the most impact on costs.

Chapter 7 provides a summary and describes future work to facilitate the commercialization of algal wastewater treatment and biofuel production system. Recommended future work includes: 1) Investigate the effects of lower HRT and long-term effects of continuous PHWW recycle; 2) Study the tailoring of the selected adsorbents and mixing ratios to address different influent wastewater qualities. 3) Develop biomass pretreatment to reduce ash content of algal biomass for improved HTL biocrude oil yield. All in all, this study proposed a novel idea of integrating different types of adsorbents into the algae cultivation system to facilitate integration with wastewater treatment and improve biofuel production. This novel adsorbent-based algal cultivation system could overcome many of the current challenges for algae systems used for wastewater treatment and sustainable biofuel production.

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1 INTRODUCTION

Intensive use of fossil fuels contributes to increasing concentrations of carbon dioxide in the atmosphere, which has been broadly implicated as a cause of global climate change. In order to address the global climate change, U.S. President Barack Obama ordered the federal government to reduce greenhouse gas emissions 28% by 2020. In addition, the U.S. Environmental Protection Agency (EPA) has set a goal for production of 36 billion gallons of biofuel by 2022 to help achieve better energy independence and reduce net CO2 emissions (Mc Carl and Boadu, 2009). The Intergovernmental Panel on Climate Change (IPCC) has also highlighted that biofuels with lower net carbon emissions are an essential strategy for mitigating global warming (Parry et al., 2007).

Algae are promising as a next generation biofuel feedstock and more broadly as a source of biomass and can produce a variety of desirable biochemical products (Chisti, 2008). Compared to other terrestrial biofuel crops, algae have much higher biomass productivity per unit area because of higher photosynthetic efficiency (Lundquist et al., 2010). Secondly, unlike corn for ethanol, algae are not a major food crop and can be grown on non-arable lands, which reduces the competition between food and fuel, while also reducing the impacts of land use changes. Third, as algae grow photosynthetically, they sequester CO_2 and can uptake excess nutrients from water, which provides opportunities to combine algal culture systems with wastewater treatment or power plant emission treatment systems (Clarens et al., 2010).

Although algae is a promising biofuel feedstock, there are still several key bottlenecks limiting the development of algal biofuels. Conventional algal biofuel approaches favor high-lipid content algal species because higher lipid amounts lead to higher biodiesel productivity. However, high lipid content algae generally have slow growth rates because lipids are produced as storage products to guard against environment stress (Williams and Laurens 2010). Thus, large-scale growth of high-lipid content algal species is often contaminated by other faster growing algae, bacteria, or grazers. Another key bottleneck is that harvesting and dewatering algal biomass can be costly and consume significant energy because the final cell concentration after algae cultivation is often below 1% solid content (Mata et al. 2010). Conventional lipid extraction processes require drying the biomass above 95% solid content for effective extraction, which can consume more energy than is present in the biofuel feedstock. Supply of nutrients for algal cultivation at low cost and low environment impact is another challenge. Lundquist et al., (2010) showed that the production cost of algal biofuel with purchased nutrients will be above $400 per barrel. However, if algae cultivation systems are integrated with wastewater treatment, the net cost of algal biofuel can be reduced to as low as $28 per barrel after subtracting out a credit for the value of water treatment benefits (Lundquist et al., 2010).

To address the challenges listed above, the environment-enhancing energy (E^2-Energy) process had been proposed (Zhou et al., 2013). As shown in Figure 1.1, E^2-Energy integrates algal cultivation and hydrothermal liquefaction (HTL) for simultaneous biofuel production and wastewater treatment. The process scheme starts with solid-liquid separation of an incoming organic biowaste stream, such as municipal wastewater, livestock manure, or food processing residuals. The concentrated biosolids portion of the biowaste is converted into biocrude oil through HTL, while the dilute liquid portion of the biowaste and the post-HTL aqueous product are fed to an algae cultivation system. Algae then uptake nutrients from these wastewaters and produce biomass. The algal biomass is collected and converted into more biocrude oil via HTL. The major benefit of the E^2-Energy is the ability of recycling wastewater nutrients multiple times within the system. The DOE National Algal Biofuel Technologies Roadmap (2010) highlighted the need for recycling wastewater nutrients because the total wastewater nutrient flows in the US are insufficient to support large-scale algal production in the basis of one-time use of nutrients. By recycling the nutrients within the E^2-Energy system, it is estimated that three to ten times more biofuel can be produced compared to one-time use of nutrients (Zhou et al. 2013).

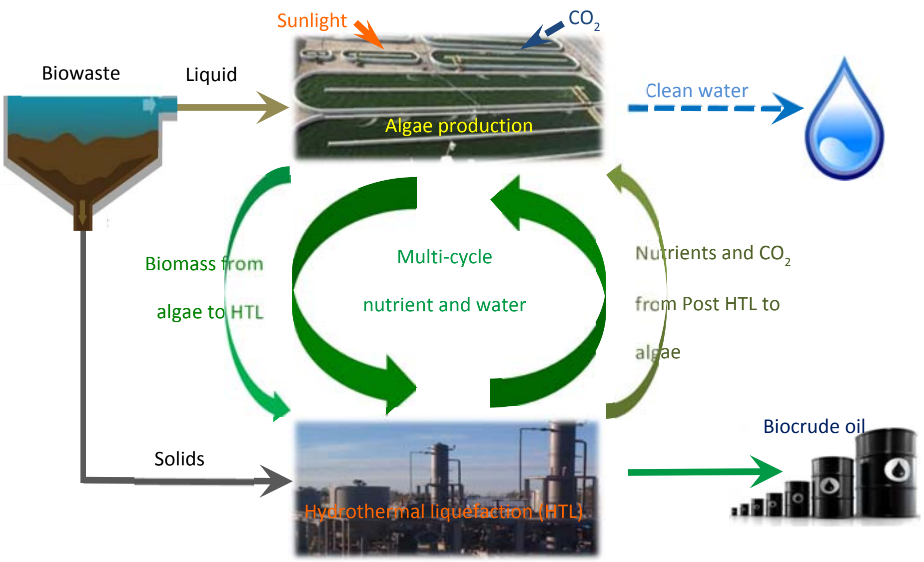


Figure 1.1 Environmental Enhancing Energy Process Scheme

Although combining algae cultivation with wastewater treatment facility has been identified by several researchers and regulators as a promising approach, there are still several challenges for using algae as a biological wastewater treatment process. First, the treatment efficiency of an algal wastewater system is more variable than conventional biological treatment using activated sludge. For instance, Garcia et al. (2005) studied the water treatment difference of an algal raceway pond system between midday and dawn. The results suggest that the diurnal cycle influences system performance, including a reduced rate of nitrification and increased effluent ammonia concentrations by up to 50% during the nighttime. Second, the turbidity of wastewater limits the light path into wastewater systems, which also reduces photosynthetic efficiency. Third, compared to conventional wastewater treatment systems, algae cultivation systems require more land area. Most algal cultivation systems usually operate at four to seven days of hydraulic retention time (HRT), whereas conventional wastewater treatment systems typically use an HRT of two days or less. In addition, relatively shallow algae cultivation systems designed to maximize sunlight inputs would require much larger land area than conventional biological treatment (Shoener et al., 2014).

To address the important issues listed above, this study investigates a novel approach using adsorbent-based algae cultivation that can improve the efficiency and reliability of integrated systems providing both wastewater treatment and algal biomass production at a reasonable cost. Chapter 3 examines the benefits of integrating different types of adsorbents into an algal wastewater treatment system using bench-scale sequencing batch reactors. Chapter 4 used a commercially available rotating algal biofilm system to evaluate potential technical barriers of using algae to treat swine wastewater and subsequent conversion of the wet mixed biomass to biocrude oil via hydrothermal liquefaction (HTL). Three different hydraulic retention times (HRT) were used to study the effects of different nutrient loading rates on nutrient removal and biocrude oil yield. The results were used to develop an optimum operation strategy for producing maximum algal biofuel and achieving high nutrient removal efficiency. In Chapter 5, the long-term benefits of integrating adsorbents into algal wastewater treatment system were investigated. This chapter also tested the ability of adsorbents amended system under continuous recycling of HTL aqueous product (PHWW). Chapter 6 reports a techno-economic analysis for three different scenarios of algal wastewater treatment system coupled with biofuel production and nutrient recycling methods. The results showed wastewater treatment credits could potentially cover all the costs for biofuel production. Sensitivity analysis suggested that the HRT of the system and the biocrude oil yield were the most sensitive factors.

2 LITERATURE REVIEW

2.1 Algae for Nutrient Remediation

Nutrient removal is becoming an important issue for wastewater treatment plants because of increasing concerns about the impacts of nutrients on the water bodies receiving wastewater treatment effluents. Many studies have shown that using algae for wastewater treatment is advantageous over conventional biological process due the ability of uptake nutrients without presence of organic carbon (Debabrata, 2015). The nutrient removal rates of algal wastewater treatment systems are a function of algae growth rate and the N and P content in harvested biomass. The nitrogen content of algae ranges from 1% to 14% of algal dry weight and phosphorus ranges from 0.05% to 3.3% (Richmond, 2004). Many different algal species have been tested for nutrient removal in various types of wastewater including Phormidium laminosum, Chlamydomonas, Scenedesmus and Chlorella. Sawayama et al (1998) reported Phormidium laminosum effectively removed 48.7% of N and 99.7% of P in secondary treated sewage wastewater in 2 days. Godos et al. (2010) showed Chlorella sorokiniana removed 78.6% of N and 45% of P from piggery waste after 8 days of treatment. Tam and Wong (2000) reported removal of nitrogen and phosphorus by immobilizing Chlorella vulgaris in simulated wastewater, and found that 100% nitrogen removal was achieved with initial nitrogen concentration lower than 20 mg/L, and 93.9% of phosphorus removal in 1 day HRT.

Growth of algae along with bacteria can enhance the remediation of the wastewater due to a symbiotic relationship (Sriram and Seenivasan, 2012). For instance, the algae turf scrubber (ATS), has been reported to achieve 40-98% nitrogen removal and 40-90% phosphorous removal in dairy and swine manure (Pizarro et al., 2006).

2.2 Algae for Organic Removal

Microalgae have been used for N and P removal after most of the organics have been removed from wastewater by conventional secondary treatment such as activated sludge (Lavoie and Delanoue, 1985; Martin et al., 1985). However, some recent studies have also reported that significant organic removal can be achieved by algae (Dilek et al., 1999; Hodaifa et al., 2008; Jail et al., 2010; Kamjunke et al., 2008).

Algae can take up organics like heterotrophic bacteria; however, the way they assimilate organics is more complicated. Algae can be classified as autotrophic algae, heterotrophic algae, mixotrophic algae, and photoheterotrophic algae (Neilson and Lewin, 1974; Stewart, 1974). Heterotrophy in algae implies the capacity for sustained growth and cell division in the dark, which appears to occur exclusively by aerobic dissimilation. They live just like heterotrophic bacteria-during respiration of substrate, oxygen is consumed and carbon dioxide is evolved. Except some colorless algae spices, e.g., Prototheca zopfii, that are obligate heterotrophs, most heterotrophic algae can also grow photoheterotrophically. Mixotrophy occurs in a few algae that may have an impaired capacity to assimilate carbon dioxide in the light. Thus, mixotrophic algae require a supply of organic carbon even for growth in light. As a general rule, carbon dioxide is simultaneously assimilated in smaller amounts than that needed for phototrophic growth. Photoheterotrophy (photoassimilation) can be found in many algae. Many algae are unable to grow heterotrophically in the dark, but they are able to incorporate certain organic compounds into cellular material, including lipids, in the light. Many algae, such as Chlamydonomas, can also assimilate exogenous acetate into lipids. Some algae are even able to incorporate long-chain fatty acids into lipids without their prior degradation (Neilson and Lewin, 1974).

Although assimilation of organic substrates by algae are well established under certain laboratory conditions, algae generally have low affinity for most of the substrates to compete effectively with other fast growing heterotrophic organisms (Neilson and Lewin, 1974). The symbiotic relationship between algae and bacteria can support the aerobic degradation of various organic contaminants. Table 2-1 summarized the organic removal from literature. O2 produced by algae can be used by heterotrophic bacteria for mineralizing organic pollutants, and the CO2 released from bacterial respiration can be used by algae in photosynthesis. Mixed algal-bacterial wastewater treatment system is receiving increasing attention for two reasons. First, photosynthetic aeration can decrease the cost of mechanical aeration which accounts for more than 50% of the total energy consumption of typical aerobic wastewater treatments (Metcalf and Eddy et al., 2003). Second, algal biomass is promising as a potential biofuel feedstock (Rodolfi et al., 2009; Li et al., 2008; Chisti, 2007; Gouveia and Oliveira, 2009; Mata et al., 2010).

However, there are some challenges in combining algae and bacteria to treat wastewater, especially in keeping a balance between these two communities in order to achieve both decent organic and nutrient removal. First, algae are more sensitive to various organic pollutants and heavy metals (Muñoz and Guieysse, 2006), which are common in various wastewater streams. Second, increased turbidity resulting from bacteria growth affects light delivery to algae. Furthermore, heterotrophic bacteria generally grow faster than heterotrophic algae (Kamjunke et al., 2008) and can outcompete algae. Finally, algal uptake of pollutants and nutrients is generally more sensitive to changes in environmental conditions such as temperature and sunlight. Therefore, the algal-bacterial combination for wastewater treatment must be carefully designed or controlled to provide a proper balance between them (Zhou Y., 2015).

Table 2-1 Algae for organic remediation

Organic pollutants	Wastewater	Experimental system	Microorganisms	Removal Efficiency	Reference
Color and organics	wood-based pulp and paper industry wastewater	1000 ml glass jae, batch experiment	Mixed culture of algae and bacteria	58% COD, 84% color and 80% absorbable halides	Tarlan et al., 2002
Color	pulping effluent	1000 ml glass jar	Mixed culture of algae and bceria	80% color removal	Dilek et al., 1999
BOD	domestic wastewater	3 m x 1 m x 0.09 m pilot scale pond	Mixed culture of algae and bacteria	85% of BOD removal	Zimmo et al., 2002
BOD	Primary effluent of domestic wastewater	5 ha high rate pond	Mixed culture of algae and bacteria	51% of BOD removal	Craggs et al., 2012
BOD/COD	2~6% dairy effluent	500 ml batch	Chlorococcum sp.	3day:COD 0%, BOD 75%, 15 day:COD:80%, BOD:95%	Beevi and Sukumaran, 2014
COD	Anaerobic digested flushed dairy manure	0.5m x 0.36 m x 0.4 m plastic container	Floating aquatic macrohytes and bacteria	80% of COD removal	Sooknah and Wikie, 2004
Glucose	Oxidation pond	250 ml flasks	*Scenedesmus obliquus* and bacteria	0.7 mol/mg per h	Abeliovich and Weisman, 1978
Acetonitrile	mineral salt medium with acetonitrile	600 ml stirred tank reactor	C. *sorokiniana* and bacteria	2300 mg/l/d	Murioz et al., 2005
Black oil	Black oil wastewater	100 L tnk	Chorella/Scenedesmus/ Rhodococcu	Oil spills 96% Phenols 85%	Safonova et al., 2004
Phenanthrene	0.2L silicone oil	2L stirred tank reactor	C. *sorokiniana* , *Pseudomonas migulae* and bacteria	8-36 mg/L/h	Munoz et al., 2005
Phenol	Coking factory wastewate	600 ml stirred tank reactor	C. *vulgaris* / *Alcaligenens* sp. and bacteria	90%	Tamer et al., 2006

2.3 Adsorbents for Wastewater Treatment

2.3.1 Adsorbent processes and models

Adsorption is a process that ions or molecules from gas or liquid accumulate onto a solid surface. Any substance that is being removed from the liquid or gas phase is referred to as the adsorbate, and the adsorbent is the media onto which the adsorbate accumulates. Adsorption is a consequence of surface energy. It can be categorized as physisorption which the bonding of adsorbate depends on the Van der Waals force; and the chemisorption occurs when the adsorbate bonding depends on covalent force (Metcalf & Eddy et al., 2003). Physisorption is a non-specific and a reversible process while chemisorption is adsorbate specific and irreversible. There are four stages for adsorbate from the bulk liquid phase to be adsorbed onto an adsorbent surface. 1.) Mass transfer of the adsorbate ions or molecules across the external boundary layer towards the solid adsorbents. 2.) Adsorbate molecules transport from the adsorbent surface into the active sites by diffusion. 3.) Solute molecules adsorption on the active sites on the interior surfaces of pores. 4.) Migrate on the pore surface through surface diffusion. The pore structure and specific surface area are the most important physical properties that determines adsorption capacity and adsorption rate of the adsorbents.

Adsorption isotherm describe the quantity of adsorbate adsorbed per unit mass of adsorbent as a function of the equilibrium concentration in the solution. At given temperature, the relationship between the equilibrium concentration of the adsorbate and the adsorbed materials on adsorbents is called the adsorption isotherm. The most common isotherm equations used to describe the experimental isotherm data were developed by Freundlich, Langmuir, and Brunauer, Emmet, and Teller (BET isotherm). Of the three, the Freundlich isotherm is used most commonly to describe the adsorption characteristics of the activated carbon used in water and wastewater treatment.

2.3.2 The application of activated carbon in wastewater treatment

Activated carbon has a wide variety of applications for liquid phase treatment: food processing, preparation of alcoholic beverages, decolorization of oils and fats, product purification in sugar refining, purification of chemicals (acids, amines, glycerin, glycol, etc.), enzyme purification, decaffeination of coffee, gold recovery, refining of liquid fuels, and purification in the personal care, cosmetics, and pharmaceutical industries. Among these applications, water treatment accounts for more than 70% of the liquid-phase activated carbon demand in industrialized contries (Rodriguez-Reinoso et al., 2001).

There are two main size classifications of activated carbon: powdered activated carbon (PAC), which typically has a diameter of less than 0.074 mm (200 sieve) and can be added directly to the activated sludge process or other solids contacting processes. Granular activated carbon (GAC), which has a diameter greater than 0.1 mm (~140sieves), is generally used in filtration applications (Asano, 2007). PAC has the advantage of faster adsorption rates, but has disadvantages associated with disposal because it is more difficult to separate from wastewater biosolids and sludge (Faust and Aly, 1987).

Activated carbon has been used in both municipal wastewater treatment and industrial wastewater treatment. The primary purpose of using it for municipal wastewater treatment was to facilitate beneficial reuse of wastewater for industrial cooling water, irrigation of parks, etc. It has also been suggested for removing micropollutants in recent years, such as endocrine disruptor and pharmaceuticals, as more focus has been put on the potential hazards of these micropollutants to the ecosystem and human health (Snyder et al., 2007; Servos et al., 2005). The main goal of using activated carbon in industrial wastewater treatment is to meet stringent regulations for discharge into receiving waters (Faust and Aly, 1987).

There are a variety of locations within the conventional wastewater treatment scheme where activated carbon has been used. Activated carbon treatment can be placed after various physicochemical treatment steps such as coagulation/clarification, filtration, and dissolve air floatation, or it can be used as a tertiary or advanced treatment step subsequent to biological treatment for removal of refractory organics. Sometimes it has also been used prior to biological treatment to remove compounds that might be toxic to biological system. It can also be integrated directly into a biological treatment reactor, which can result in the removal or sequestering of refractory and inhibitory compounds (Metcalf & Eddy et al., 2003; Çeçen and Aktas, 2011).

2.3.2.1 The removal of pollutants by physicochemical adsorption

As a porous carbonaceous adsorbent, activated carbon can remove a broad variety of organic solutes as well as some inorganic solutes from wastewater by physicochemical adsorption. This pollutant removal mechanism has been used widely especially in removing dyes (Namasivayam and Kavitha 2002) and heavy metals (Amuda et al., 2007) from industrial wastewater, as well as removing refractory compounds and micropollutants as a tertiary/polishing treatment for municipal wastewater (Snyder et al., 2007). The adsorption process requires little or no energy inputs and generally requires only seconds or minutes of contact time with the water, which is significantly faster than the net rates of biological processes (Metcalf & Eddy et al. 2003). The group of organics that are generally amenable to adsorption onto activated carbon include pesticides, herbicides, aromatic solvents, polynuclear aromatics, chlorinated aromatics, phenolic, chlorinated solvents, high-molecular-weight (HMW) aliphatic acids and aromatic acids, HMW amines, and aromatics amines, fuels, esters, ethers, alcohols, surfactants, and soluble organic dyes. Compounds having low molecular weight (LMW) and high polarity, such as LMW amines, nitrosamines, glycols, and certain ethers, are not amenable to adsorption (Çeçen and Aktas 2011).

The adsorption process takes place in four steps: 1) bulk solution transport, 2) film diffusion transport, 3) pore and surface transport, 4) adsorption (or sorption). The adsorption step involves the attachment of the material to be adsorbed to the adsorbent at an available adsorption site. Adsorption can occur on the outer surface of the adsorbent and in the macropores (>50 nm), mesopores (2-50 nm), micropores (micro-pore <2 nm). But the surface area of the macro and mesopores is small compared with the surface area of the micropores, and the amount of material adsorbed there is usually considered negligible. Many factors are known to have important influence on adsorption process including the material carbon is made of, carbon surface functionalities, pH value, oxygen availability, addition of electrolytes, etc.. Optimization of adsorption processes can generally enhance the removal of a specific compound (Bansal and Goyal 2010).

2.3.2.2 The integration of activated carbon with biological treatment

Adsorption and biological processes can take place in separate unit processes, or they can happen in the same reactor. The latter form of integration often offers synergy such that a higher degree removal is achieved than from adsorption or biodegradation alone, and it will be the focus of this literature review. For many pollutants that are considered slowly biodegradable or even nonbiodegradable, this integration may enhance the effectiveness of biological degradation. A typical configuration of using activated carbon in wastewater treatment is shown as Figure 2.1 (using PAC as an example). There are mainly two forms, as described below.

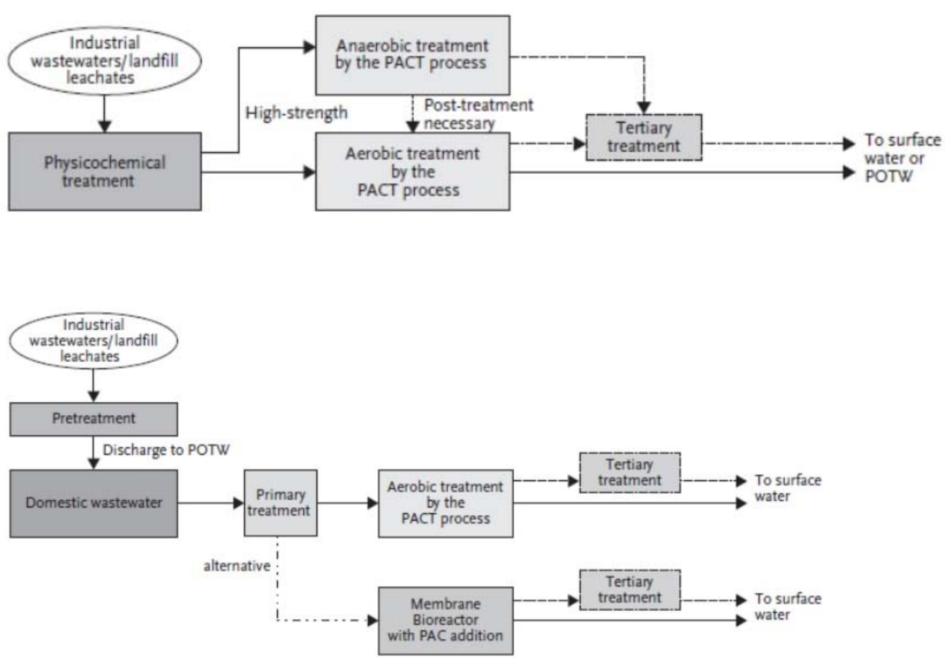


Figure 2.1 PAC application in wastewater treatment (Cecen and Aktas, 2010)

The powdered activated carbon treatment (PACT) process is a modified version of the conventional activated sludge process by the addition of PAC. It is an effective alternative for the removal of biodegradable and nonbiodegradable compounds, such as organic halogens (Orshansky and Narkis 1997; Bornhardt et al., 1997). PAC has also been integrated into membrane bioreactors (MBRs) as it can enhance contaminant removal and also prevent membrane biofouling (Munz et al. 2007). The PACT process is often employed in secondary treatment of high-strength industrial wastewaters and landfill leachates (Foo and Hameed 2009; Walker and Weatherley 1999; Pirbazari et al. 1996).

The biological activated carbon (BAC) process is basically a GAC filtration bed where a large amount of aerobic biomass is accumulated or immobilized to exert the adsorption and biodegradable roles simultaneously. Adsorption sites in GAC become saturated with adsorbate and the activated carbon loses its initial effectiveness over time. Then the biofilm developed on GAC and the filter bed becomes biologically active due to the presence of bacteria which inhabit the pores of GAC. The biological reaction ensures the filter bed continuous to remove organic by metabolic process. Although the removal of organic is significant by biological activities, it is still less than that achieved by new GAC. However, the effective life of BAC is often over 10 years whereas the life of a GAC filter relying on adsorption alone can be as short as 3 months. This results in a long operating time of the carbon before having to be regenerated and thus a low treatment cost (Xiaojian et al., 1991). BAC filtration is also used to some extent for the elimination of inorganics such as ammonia, perchlorate, and bromate (Walker and Weatherley, 1999). Both the PACT and BAC system has also been adopted for anaerobic process (Park et al., 1999; Bertin et al., 2004).

The integration of activated carbon process enhances the degradation of slow-degrading compounds. Upon adsorption onto activated carbon, the retention time of an organic substance in a biological system is considerably increased. For example, in the PACT process, dissolved organics adsorbed on activated carbon are retained in the system for about 10-50 days, while in conventional biological systems they will be kept for a period equal to the hydraulic retention 16 time (HRT), typically 6-36 hour. The retention of organics may even be longer in a BAC reactors since the GAC is kept for a very long period of time in the reactor. The long retention of the pollutants on carbon surface enables the acclimating of attached and suspended microorganisms to these organics, eventually leading to their efficient biodegradation (Çeçen and Aktas, 2011; Xiaojian et al., 1991)

In summary, adsorbents can provide fast physicochemical capture of slowly-degrading and toxic compounds to accommodate the time needed for biological removal. Adsorbents can improve effluent quality by maintaining consistently lower effluent concentrations of organics, and then slowly release the organics as they are taken up by the microbes. Therefore, the adsorption process is much less sensitive to upset and natural variations in operating conditions, and can temporarily store organic substrates while microbes are adapting to changed conditions. Adsorbents provide benefits such as buffering against shock loadings, toxic compounds, and fluctuations in biological performance due to temperature, pH, sunlight intensity, etc. This will eventually improve reactor stability and effluent water quality, which is obviously important for wastewater applications.

2.4 HTL of Algal Biomass

Many past studies have shown that both wet algae and wastewater biosolids can be effectively converted into a bio-oil crude via Hydrothermal liquefaction (HTL) (He et al., 2000, Yu et al., 2011), which lowers the net energy demands associated with dewatering, drying and extraction. Specifically, HTL can be performed on biomass with a water content of up to 85%, and it produces a self-separating bio-oil phase that has a much better net energy balance than current algal biofuel approaches. Laboratory HTL reactors without heat exchangers typically achieve energy recovery ratios (E_{out}:E_{in}) above 3:1, which compares the energy output of the HTL biocrude oil to the process heating energy input. HTL uses elevated temperatures (200–400˚C), and pressures (10-15 MPa) to convert organic solids in the feedstock into four products: (1) bio-crude oil, (2) bio-char solid residue, (3) a gas rich in carbon dioxide, and (4) wastewater with high soluble concentrations of both organics and nutrients. HTL does not just extract oil, but also converts proteins and carbohydrates into oil, so the oil yield is much higher than the lipid content of the algal feedstock (Peterson et al. 2008; Minowa et al., 1995). Therefore, a variety of feedstock including bacteria, wastewater sludge (Itoh et al., 1994; Yokayama et al., 1987; Suzuki et al., 1988), and fast-growing, low-lipid content algae (Yu et al., 2011; Vardon et al., 2011) have all been successfully converted into bio-crude oil via HTL. Thus, HTL resolves the contamination problems associated with current algal biodiesel paradigms. Additionally, HTL resolves the energy balance issues because water serves as the reaction medium for HTL, which avoids the need for biomass drying. Additionally, the bio-crude oil product self-separates from the wastewater product. Thus, wet algal biomass feedstock (20-30% solids content) are acceptable for HTL, which minimizes the energy used for dewatering algae and greatly improves both the net economic and energy returns for algal biofuels.

Post-hydrothermal liquefaction wastewater (PHWW) is a high-strength wastewater that can accumulate most of the feedstock nutrients (approximately 80%) and some of the organics (up to 40%) (Yu et al. 2011), which provides a significant opportunity for nutrient and carbon recycling. PHWW recycled back to the algae culturing system can allow for multiple cycles of algae growth on each aliquot of incoming nutrients, which maximizes bio-energy production per unit of nutrient inputs. This approach has been investigated in recent studies using HTL wastewater (Jena et al., 2011; Biller et al., 2012; Du et al., 2012) and an earlier study suggested a similar approach but used a recondensed wastewater from gasification (Minowa and Sawayama, 1999). These studies show that nutrients in wastewaters from thermochemical conversion processes can be used for algae cultivation, but that significant dilution was required (50-500 times). These studies did not however identify a viable and sustainable source of dilution water and raised other important questions about how this nutrient recycling can be incorporated into an algae biofuel production system. This study addresses these issues in pursuit of an optimized system integrating algal wastewater treatment and bioenergy production including original process modeling to quantify the specific benefits of nutrient recycling and analyze the national implications for sustainable biofuel production.

3 INTEGRATING ADSORBENTS INTO ALGAL WASTEWATER TREATMENT SYSTEMS TO IMPROVE WATER QUALITY AND BIOMASS PRODUCTIVITY

3.1 Introduction

Algal biofuels have been identified as one of the most promising alternatives for replacing the petroleum used in transportation fuels (Chisti et al., 2008). The current predominant approach to algal biofuels is based on selectively growing high-oil algae and then extracting the algal oils for conversion to biodiesel via transesterification. However, recent studies suggest that only algae cultivated in wastewater can facilitate biofuels that are cost-competitive with net environmental benefits (Clarens et al., 2010; T J Lundquist, 2010). The National Algal Biofuels Roadmap has also highlighted several key advantages for integrating algal cultivation with wastewater treatment, such as better water sustainability, low-cost nutrient inputs, and lower net biomass production costs by using wastewater infrastructure (DOE, 2010). However, there are still some bottlenecks that limit the development of algae-based wastewater treatment systems. For instance, the cost of harvesting algal biomass from dilute cell suspensions at the end of the treatment process is a major challenge due to relatively low cell concentrations (Ruiz-Marin et al., 2010). Furthermore, Rafeal et al. (2009) reported phenolic compounds and heavy metals in sewage wastewater can inhibit the growth of algae (Órpez et al., 2009). Picot et al. (2009) reported decreased water treatment performance of a high rate algal pond (HRAP) at night due to photorespiration and pH changes. The ammonia removal percentage can drop from 95% to 75% between day and night cycles. Therefore, it is important to search for a new method to address these problems.

On the other hand, adsorbents are widely used for removing various organics and heavy metals in wastewater treatment. Activated carbon is the most commonly used adsorbent in wastewater treatment. Powdered activated carbon (PAC) and granular activated carbon (GAC) are the two main forms of activated carbon used in wastewater treatment (Gupta et al., 2009). GAC is more adaptable in wastewater treatment applications because of the ease of separation of the adsorbent from the bulk liquid. Activated carbon is able to adsorb different types of pollutants such as metal ions, phenols, pesticides, and many other chemicals (Pollard, Fowler, Sollars, & Perry, 1992). Zeolites and ion exchange resins are selective adsorbents that are capable of reversible ion exchange reactions. Zeolite is usually used for removing ammonium from wastewater effluent. Zeolite also serves as a physical carrier for nitrifying bacteria to improve the nitrogen removal rate (Lahav, 2000). Although adsorbents are capable of improving water quality, the cost for regeneration is a major concern for using them. The common adsorbent regeneration methods are thermal or chemical treatment. Activated carbon can be regenerated at 500 – 900^{o}C in an inert atmosphere (Gupta et al., 2009). Zeolite can be regenerated in 8% NaCl solution (Luo et al., 2011). Both regeneration methods either consume significant amounts of energy or require large quantities of brine solutions, which are important limitations for the application of adsorbents in wastewater treatment.

This study explores the benefits of integrating bioregenerable adsorbents into an algal wastewater treatment system. Adsorbents can act as an attached growth carrier that enhances the development of biofilm in the system. The growth of biofilm can help algal wastewater treatment systems in two ways. The first one is it allows the system to separate solid retention time (SRT) from hydraulic retention time (HRT). It is especially important for continuous systems since it allows the system to maintain higher cell density at low HRT thus the system can treat more wastewater with the same area. The second benefit is it reduces the difficulty of harvesting biomass. Biofilm systems are able to collect biomass through gravity settlement without flocculants. In addition, adsorbents can prevent the damage from toxic compounds or shock loading. Once the toxic compounds or excess nutrients enter the system, they will be first adsorbed by adsorbents because adsorption rates are faster than most biodegradation rates until the adsorbents approach equilibrium with bulk water (Aktaş and Çeçen, 2007). Moreover, algae and microorganism are able to at least partially bioregenerate adsorbents and thus prolong the service life of adsorbents and making them more cost effective in wastewater treatment.

3.2 Material and Methods

3.2.1 Algae cultivation conditions

Mixed algal cultures were collected from the secondary clarifier of the local wastewater treatment plant (Urbana-Champaign Sanitary District). After collection, mixed algal samples were inoculated into 150 ml containers and placed on a shaker table at room temperature under constant fluorescent light. Filtered primary wastewater from the same wastewater treatment plant was used as growth medium. Algal cultures were rotated at 150 rpm, 25 °C with a light intensity of 50 μmol photon m^{-2} s^{-1}. After 3 days of cultivation, the dominant species were identified under microscope. Chlorella sp. and Scenedesmus sp. were the major species found in the sample. The characteristics of the filtered wastewater were as follows: soluble chemical oxygen demand (SCOD): 125 ±3 mg/L, total nitrogen: 21±0.7 mg/L, NH_3−N: 14 ± 0.5 mg/L.

3.2.2 Adsorbent preparation

Natural Zeolite NV-Na* Ash Meadows Clinoptilolite was obtained from St. Cloud Mine (St. Cloud Zeolite, Winston, NM). The material arrived preprocessed to a standard sieve sizing of 14 x 40 mesh (between 0.4 to 1.4 mm). Before use, the zeolite was rinsed thoroughly with deionized water (DI). For conditioned samples, zeolite was then soaked in 10 % saltwater overnight and rinsed once more with DI water before use. Filtrasorb®400 granular activated carbon (CalgonCarbon, Pittsburgh, PA) was used for this study. Isotherms for the zeolite and GAC adsorbent were determined by batch testing (Cooney et al.,1998).

3.2.3 Sequencing batch experiments

500 ml CELLSTAR® flat cell culture flasks (Greiner BioOne, NC, USA) were used for sequencing batch experiments. Liquid volume was loaded to 200 ml for better mixing on the shaker. All of the test conditions are summarized in Table 3-1. Four different types of control conditions were used (wastewater only and wastewater plus either zeolite, GAC, or algae) and three different test conditions with both algae and adsorbent(s) (Algae/Zeolite, Algae/GAC and Algae/Mixed adsorbents) were conducted to investigate the effects of adsorbents on algae growth and water quality. These cultivations were carried out in triplicate. 20 ml samples were collected at hour 0, 6, 8, 12, and 18 of each day. 100 ml of filtered primary wastewater were refilled each day after the sample taken at the 6^{th} hour. 3 ml of 0.1M $NaHCO_3$ were added into the flasks at the same time as the inorganic carbon supplement. The amount of zeolite and GAC added were designed to be effectively maintaining effluent NH_3-N and COD concentration below 4 mg/L and 20 mg/L for 48 hours under abiotic conditions. Specifically, 5 g of zeolite and 2g of GAC were added into 200 ml of liquid volume in each reactor and the adsorbents were neither removed nor replaced during the experiment.

Table 3-1 Experimental condition of different sequencing batch test groups

Test Groups	Wastewater	Algae Innoculum	Light/Dark Cycle	Zeolite	GAC
Wastewater	200 ml	-	0/24	-	-
Zeolite	200 ml	-	0/24	5 g	-
GAC	200 ml	-	0/24	-	2 g
Algae	180 ml	20 ml	12/12	-	-
Algae/Zeolite	180 ml	20 ml	12/12	5 g	-
Algae/GAC	180 ml	20 ml	12/12	-	2 g
Algae/Mix	180 ml	20 ml	12/12	5 g	2 g

3.2.4 Water quality analysis

Water samples were first filtered using 0.45µm pore size syringe filters (Whatman puradisc-25mm) to remove cells and particles. Then, soluble chemical oxygen demand (SCOD) was determined by visible light absorbance after dichromate digestion according to standard methods (Clesceri et al. 1999) with a HACH Model DR/2010 spectrophotometer. Total soluble nitrogen was measured using the HACH TNT Persulfate Digestion Method No. 10072. Ammonia nitrogen was determined according to HACH Nessler Method No. 8038.

3.2.5 Biomass evaluation

Algal growth was monitored using optical density at 680 nm (OD_{680}) (Das et al., 2011). Suspended biomass and attached biomass on adsorbents were measured as volatile suspended solids (VSS) and volatile solid (VS) according to standard (Eaton and Franson, 2005). Calibration curves for OD_{680} and VSS were developed via regression analysis ($r^2 > 0.96$ for OD_{680} between 0.2 to 0.8).

3.3 Results and Discussion

3.3.1 pH changes with adsorbent addition

pH is one of the most important environmental factors that affects both physical and biological activities. Figure 3.1 shows the measured pH results for each of the test conditions described earlier in Table 3-1.The white and grey portions of the graph represent the light and dark cycles, respectively. The pH drops in the middle of the days were due to the refilling with fresh influent.

There are significant differences between the vials with and without algae. Test vials with algae had higher pH than the control groups without algae, and a similar phenomenon was also found in other studies (Grobbelaar, 2000; Lee et al., 1996). While algae grow photosynthetically under light, they uptake carbon dioxide from water, and this typically causes a rise of pH (King, 1970). The four groups with algae have similar trends in that pH increases during light and decreases during dark. The pH decrease is mainly due to the respiration of microorganisms releasing carbon dioxide back into the water. Diurnal pH variation is evident and is influenced by the interaction of physico-chemical and biological reactions, which can subsequently affect the performance of algal wastewater treatment systems.

The test vials with GAC and mixed adsorbents had a lower pH than test groups with zeolite and algae only ($p < 0.05$). This can be explained by the GAC enhancing the growth of bacteria in the system thus producing more CO_2, which reduced the pH in the water.

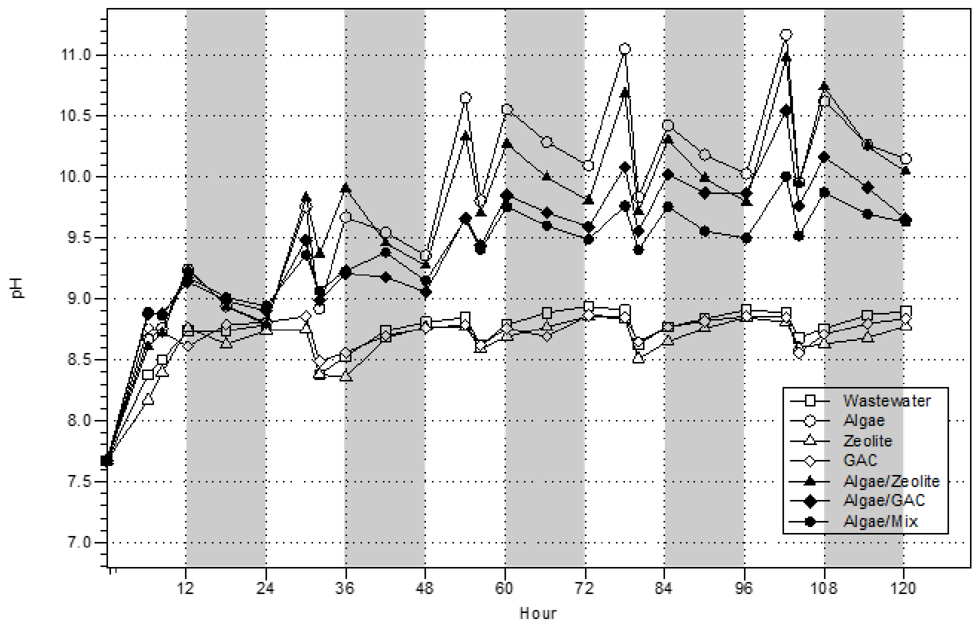


Figure 3.1 pH changes with different operating conditions

3.3.2 Optical density (OD_{680}) changes with different adsorbents addition

OD_{680} is correlated with the chlorophyll concentration in the system, which was used as a measure of the amount and growth of algae. Figure 3.2 shows the OD_{680} results for the various test conditions, which indicates that all testing conditions with adsorbents and algae had better growth rate than the control with algae alone. The vials with mixed adsorbents had the highest algae growth rate because it had both benefits of integrating zeolite and GAC. Algae/Zeolite had less algae growth than Algae/Mix but higher growth than Algae/GAC. This could be because zeolite stored ammonia, a key nutrient, when it entered system and released it back into the bulk solution after algae had depleted the available nitrogen during photosynthesis. Another possible beneficial effect of zeolite could be that it contains silicon that can release silicic acid into water and enhance diatom growth (Fachini et al., 2005). Algae/GAC had better algae growth than Algae only, which can be explained by GAC retaining organics in the system that enhanced heterotrophic microbial growth and providing additional surface area for attached growth. These heterotrophic bacteria would then produce additional carbon dioxide, which can subsequently enhance autotrophic growth.

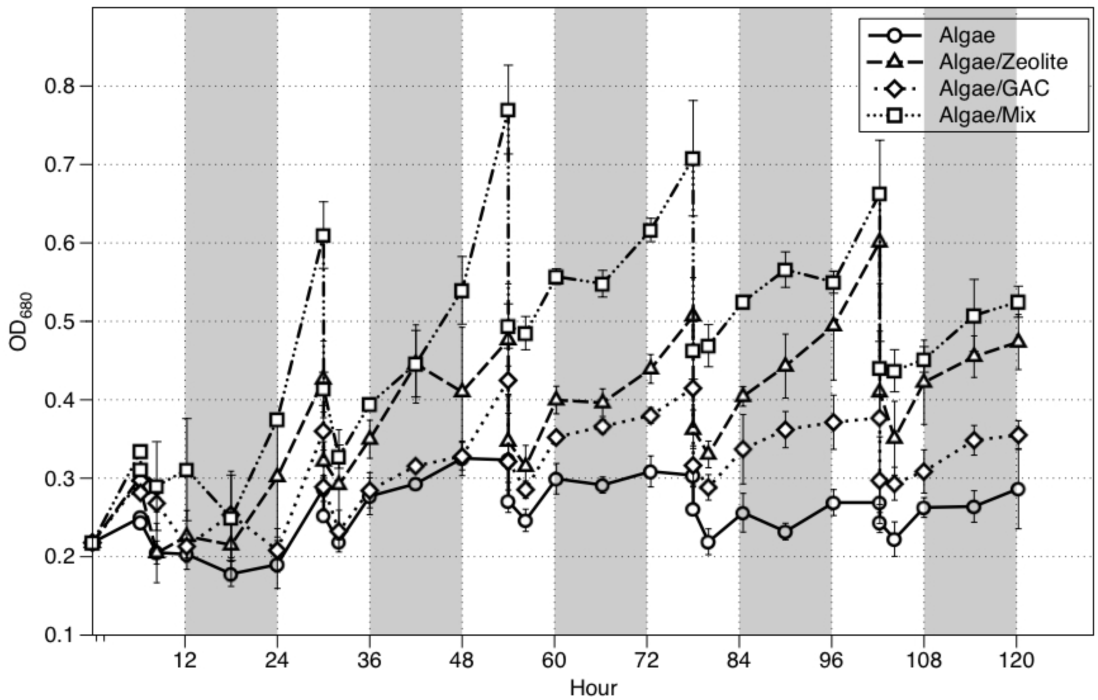


Figure 3.2 OD_{680} of the test groups with and without adsorbents

Figure 3.3 shows the total volatile solids (VS) for the four operating conditions seeded with algae. 5-day VS for suspended biomass were the sum of collected samples over 5 days based on OD_{680} and an empirical correlation developed with VS. The mass of biofilms built up on adsorbents were measured at the end of 5 day by vigorously shaking the adsorbents to scour off most of the biomass. The result showed both zeolite and GAC can not only enhance attached biofilm growth but also increase suspended algae growth. This can be explained by several factors. First, adsorbents serve as a buffer that can desorb key nutrients and substrates back into bulk solution when algae have depleted them. Second, adsorbents can remove inhibitory compounds in wastewater which can include, ammonia, organics or heavy metals (Órpez et al., 2009). Third, the biofilm can have a positive interaction with the suspended organisms such as increasing the CO_2 concentration by respiration, which can benefit phototrophic algae. The biofilm VS on Zeolite, GAC, and Mix were 54.9± 5.2, 49.2± 4.9, and 64.3± 5.1 mg. It is interesting that the biofilm VS on zeolite was higher than GAC even though the total surface area of GAC is larger than zeolite. Fachini et al. (2005) reported that zeolite can release a silicic acid into water and enhance the growth of diatoms. The mixed adsorbent condition had the most biofilm growth because it had benefits from both the GAC and zeolite.

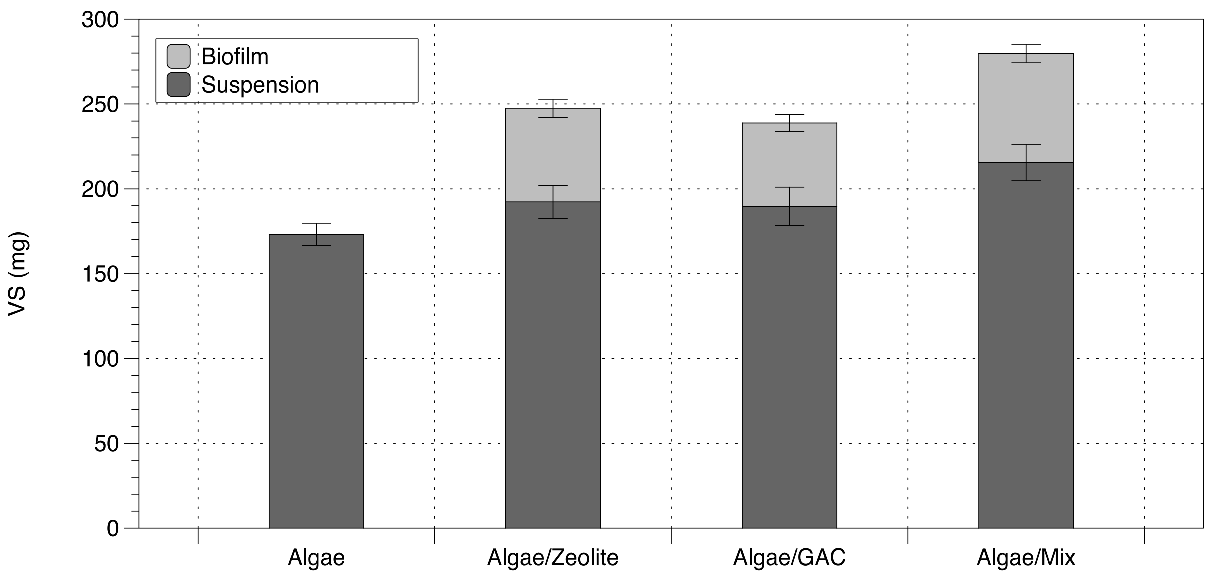


Figure 3.3 Five-day suspended and biofilm VS

3.3.3 Effect of different adsorbents on SCOD

SCOD is commonly used to represent the soluble organic concentration in water. In this system, the reduction of SCOD is mainly due to physical adsorption and microorganism assimilation. As shown in Figure 3.4, test conditions with GAC (GAC, Algae/GAC and Algae/Mix) were able to reduce SCOD concentrations faster than other test conditions after daily refilling events, which indicates the physical adsorption was the major removal mechanism.

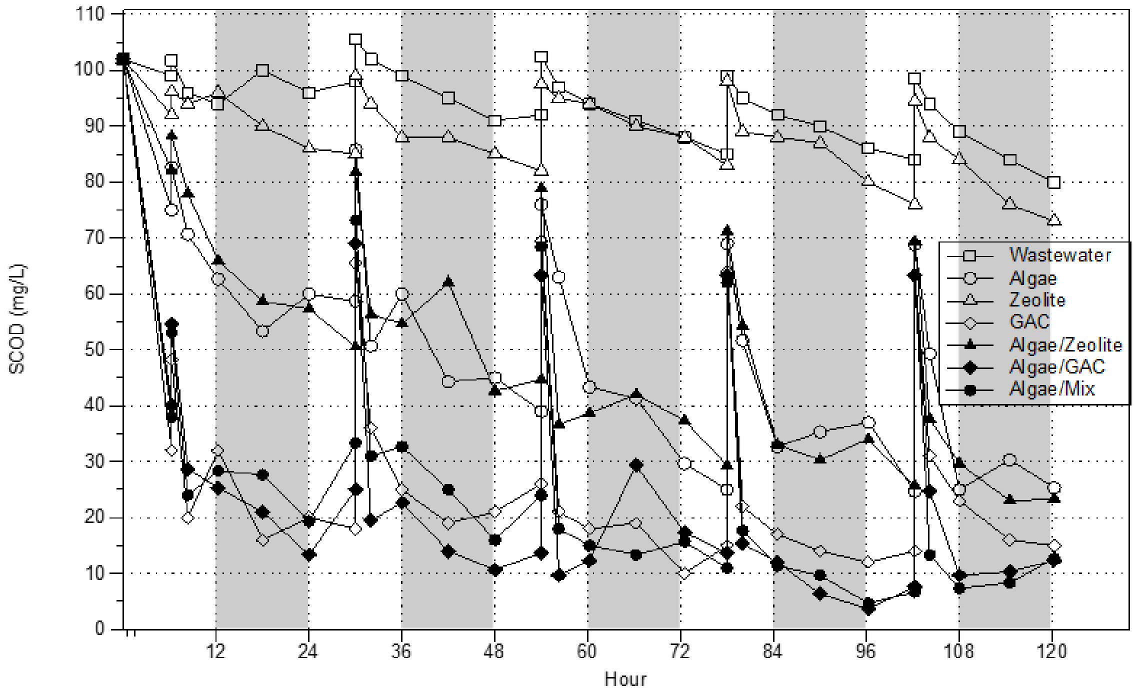


Figure 3.4 SCOD concentration of all test groups

Table 3-2 provides the SCOD average removal rate for lighted times and dark times for all test conditions, which clearly indicates the removal of individual mechanisms. The algae biological assimilation rate was 4.78 mg/L/hr. The rate of GAC physical adsorption was 6.75 mg/L/hr. Test groups with zeolite had no or little effect on the test groups without zeolite (Zeolite: 1.26 mg/L/hr, Algae/Zeolite: 5.21 mg/L/hr). This result is expected because the zeolite is considered as an ion exchange material that does not adsorb any significant amount of organics. Test groups with GAC had higher SCOD removal rate, Algae/GAC 7.81 mg/L/hr and Algae/Mix 7.69 mg/L/hr.

Table 3-2 SCOD removal rate of all test groups

	SCOD Removal Rate (mg/L-hr)	
	Light time	**Dark time**
Wastewater	1.08	0.44
Algae	4.78	0.45
Zeolite	1.26	0.63
GAC	6.75	0.62
Algae/Zeolite	5.21	0.46
Algae/GAC	7.81	0.41
Algae/Mix	7.69	0.44

3.3.4 Effect of adsorbents on ammonia nitrogen (NH_3-N)

Figure 3.5 shows the ammonia nitrogen concentration of all test conditions. The ammonia level drops rapidly for all vials with zeolite. Since physical removal is generally faster than biological removal, it suggests that most of the ammonia is first adsorbed by zeolite and then desorbed while algae uptake ammonia in the water to maintain equilibrium between adsorbed ammonia and dissolved ammonia. Considering that a high concentration of ammonia can inhibit the growth of algae, integrating zeolite into an algae cultivation system could prevent the risks associated with typical influent variability and more extreme shock loading events. This is particularly useful in the situations where the wastewater loading rate is highly variable. For example, swine farms general flush wastewater once or twice a day (Vu et al., 2007). The overall results suggest that algae is capable of partially bioregenerating zeolite because the zeolite test conditions gradually built up ammonia over time while other groups with algae kept a more stable ammonia concentration. The other synergy of integrating algae and zeolite adsorption is the growth of algae usually increases pH, which also increases the capacity of zeolite (Kithome et al.,2008).

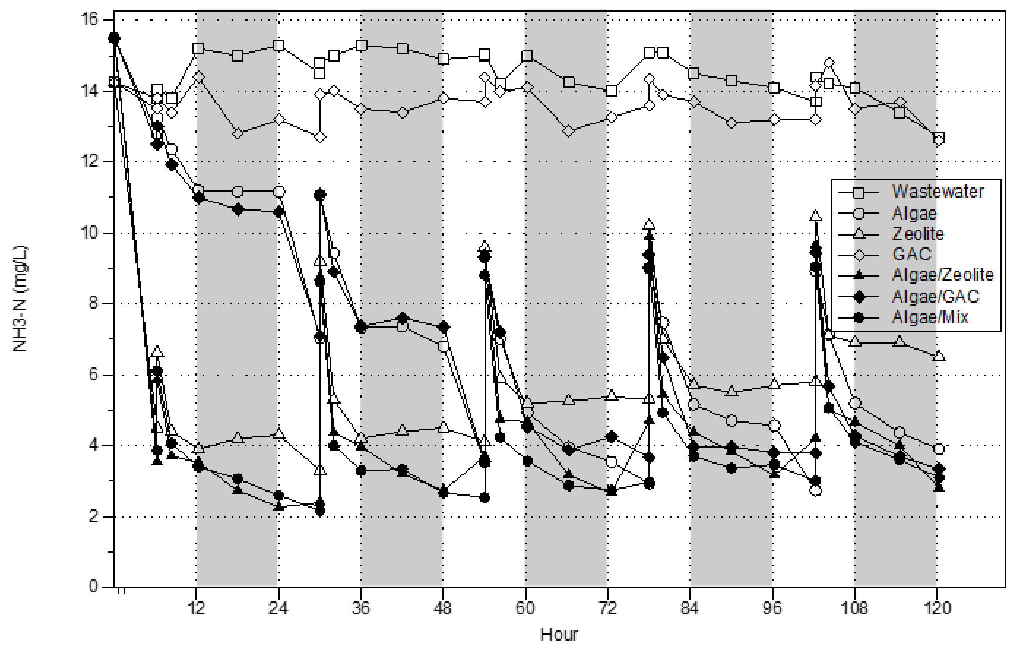


Figure 3.5 Ammonia nitrogen concentration trends over time for different operating conditions

Table 3-3 shows the average ammonia removal rate of all test conditions. Compared with the control vials with algae only (0.56 mg/L/hr), faster ammonia average removal rates were achieved during the lighted periods for all the test vials with zeolite added: Zeolite (0.71 mg/L/hr), Algae/Zeolite (0.77 mg/L/hr) and Algae/Mix (0.83 mg/L/hr). Faster removal rates provide the opportunity to increase the loading rate, which means the system could treat the same amount of ammonia in a smaller reactor volume. However, in the long-run the ammonia loading should still be matched to the bioregeneration rate to avoid complete saturation of zeolite.

According to our results, using GAC did not significantly improve the ammonia removal rate. However, Algae/GAC had slightly better removal rate than Algae only control vials. This relatively minor effect could be explained by GAC enhancing nitrifying and heterotrophic bacterial growth, which also benefited the growth of algae by providing an extra inorganic carbon source.

Table 3-3 Average ammonia removal rate of all test groups

	Ammonia Removal Rate (mg/L/hr)	
	Light time	**Dark time**
Wastewater	0.01	0.07
Algae	0.56	0.06
Zeolite	0.71	-0.01
GAC	0.04	0.06
Algae/Zeolite	0.77	0.13
Algae/GAC	0.67	0.03
Algae/Mix	0.83	0.06

3.3.5 Summary of water treatment and biomass productivity

Table 3-4 shows the summary of water treatment efficiency and biomass productivity in this study and similar works from the literature using algae to treat wastewater without adsorbents. It is clear that the zeolite and GAC used in this study can improve certain water quality parameters and biomass productivity. The Algae/Zeolite condition had the best ammonia removal percentage (81.5%) in this study, and Algae/GAC had the highest SCOD removal percentage. All of the tested conditions with adsorbents had a better TN removal percentage than algae only. Considering the fact that there is little or no denitrification under aerobic conditions, TN removal is mostly due to the extra biofilm growth and storage of nitrogen in biomass. As noted in previous literature, frequent harvesting is required to prevent the decay of biomass and the release of nitrogen back into water, which would reduce the net treatment efficiency (Strom, 2006). Comparing to other research, integrating adsorbents is able to achieve higher COD and

TN removal as well as higher biomass productivity, all at lower HRT. The lower ammonia removal percentage in this study is likely due to the relatively low ammonia concentration in influent water (14 mg/L).

Table 3-4 Summary of water treatment efficiency and biomass productivity

	HRT (Day)	Operation	COD Removal (%)	TN Removal (%)	NH3 Removal (%)	Biomass Production (mg/L/day)	Ref.
Algae	2	S.B.	77.5	47.6	74.2	173	This study
Algae/Zeolite	2	S.B.	79.4	77.8	81.5	257.2	This study
Algae/GAC	2	S.B.	89.1	76.2	77.9	238.8	This study
Algae/Mix	2	S.B.	88.8	79.4	79.5	279.8	This study
Polyculture/ Municipal Wastewater	2	S.B.	-	-	98	204.4	Woertz et al., 2009
	4	S.B	-	-	>99	212.2	
Polyculture/ Municipal Wastewater	7	C.	34.6	72.7	-	42.3	Garcia et al., 2006
	4-5	C.	38.5	52	-	49.3	
Fixed-film/Animal Wastewater	6	C.		61.58	94.29	3.5 g/m2/d	Johnson M.B., 2010
Polyculture/ Domestic Wastewater	4-8	C.	68.7	47.7	74.6	-	Picot et al., 1992

S.B.: Sequencing batch; C.: Continuous

3.4 Conclusions

Several key advantages of integrating adsorbents with algae cultivation have been demonstrated in this study. (1) Adding GAC and/or zeolite into algal wastewater treatment systems can improve effluent water quality. Specifically, the ammonia removal percentage increased from 74.2% to 81.5% after addition of zeolite; the SCOD removal percentage increased from 77.5% to 89.1% after addition of GAC; and the TN removal increased from 47.6% to 79.4% after addition of both zeolite and GAC. (2) There were significant improvements in biomass productivity for all tested conditions with adsorbents. Biomass productivity increased from 173 mg/L-d to 279.8 mg/L-d with addition of both adsorbents, resulting in higher productivity than other similar studies without adsorbents. (3) Mixing zeolite and GAC can further improved both water quality and biomass productivity than individual adsorbent addition.

In summary, this study demonstrated that adding adsorbents can facilitate the integration of algal bioremediation into wastewater treatment processes. Integrating adsorbents into algal wastewater treatment systems can yield more biomass and produce better water quality at shorter HRT compared to other algal wastewater treatment systems. Future work includes optimizing the types and ratio of mixed adsorbents for different wastewater, designing a scalable adsorbent-based algal wastewater treatment system and studying the longer-term effects of adsorbents.

4 PILOT-SCALE ROTATING ATTACHED GROWTH ALGAL WASTEWATER TREATMENT FOR SWINE WASTEWATER AND BIOCRUDE OIL PRODUCTION

4.1 Introduction

Environmental concerns associated with animal feeding operations (AFOs) have been a major issue in the United States (Eng et al., 2003). For concentrated animal feeding operations (CAFOs), the environmental issues are heightened, and states with a high concentration of CAFOs have experienced 20 to 30 serious water quality problems per year as a result of poor manure management (EPA, 2001). It is estimated that 1.2 to 1.4 billion wet tons of manure produced by livestock annually in the US, which contains at least 3 times more biosolids than is generated by all the U.S. human population (NALBOH, 2010). Currently, the most common manure management process for CAFOs in the U.S. is an anaerobic lagoon followed by irrigation on farm fields. Digested manure can be used as fertilizer or soil conditioner due to its significant nutrient content, particularly nitrogen and phosphorus. However, nutrients can also enter nearby surface water or groundwater by runoff and infiltration, which often leads to environmental problems such as eutrophication or hypoxia which can negatively impact aquatic life. Therefore, developing manure management alternatives that mitigate these environmental impacts is highly advantageous.

On the other hand, many studies have shown that algae cultivated on swine wastewater can effectively remove nutrients and potentially produce extra biomass for bioenergy. Godos et al. (2009) treated 10- and 20-fold diluted swine manure with a high rate algal pond (HRAP) using 10 days of hydraulic retention time under continental climatic conditions for 10 months. The results showed a HRAP is able to achieve COD and TKN removal efficiencies of 76±11% and 88±6%, respectively. The biomass productivity ranged from 21 to 28 g/m^2-d. However, the study showed less than 10% phosphorus removal efficiency due to the high buffer capacity of piggery wastewater that prevented orthophosphate precipitation. Min et al. (2013) developed a greenhouse-based multilayer photobioreactor for algal biomass production and swine wastewater treatment. The NH3-N, TN, COD and PO4-P reduction rates were 2.65, 3.19, 7.21 and 0.067 g/m^2-d, respectively. The areal biomass productivities ranged from 19.15 to 23.19 g/m^2-d (TSS) or 8.08 to 14.50 g/m^2-d (VSS). Although these studies showed promising alternatives for swine wastewater treatment, the cost of harvesting suspended algal biomass in these systems is a major challenge for cost-effective algal biofuel production (Ruiz-Marin et al., 2010). Molina-Grima et al. (2003) reported the cost of harvesting suspended algal biomass can account for up to 30% of the total system cost. Attached growth algal cultivation systems can mitigate this problem as the algal biofilms have higher solids content and can usually be readily dewatered by sedimentation, straining or filtration. Immobilization of algal biomass using carrageenan or alginate is one of the common attachment methods (Chevalier et al., 2000; Hameed and Ebrahim, 2007). However, the high cost of polymers inhibits the use of this technique at large scale (Hoffmann, 1998). Christenson and Sims (2012) developed a rotating algal biofilm reactor (RABR) aims to reduce soluble nitrogen and phosphorus concentration as tertiary wastewater treatment and increase algal biomass productivity for biofuels. The Algal Turf Scrubber grows filamentous algae on a plastic mesh by intermittently passing water over the surface (Adey et al., 1993). It has been used at full scale for water treatment applications, but the filamentous algae product are generally less useful for biofuels than other species (Mulbry et al., 2008).

In this study, a rotating, attached-growth, algae cultivation system was used to evaluate the techno-economic barriers of using algae to treat swine wastewater and the subsequent conversion of the wet mixed biomass to biocrude oil via hydrothermal liquefaction (HTL). Three different hydraulic retention times (HRT) were used to study the effects of varying nutrient loading rates on the removal of nutrients and the resulting biocrude oil yield. The results of this study can be used to develop an optimal operating strategy for maximizing algal biofuel yield and achieving a relatively high nutrient removal efficiency.

4.2 Material and Methods

4.2.1 Algae cultivation system

In this study, we used the commercially available Algaewheel® system made by OneWater Inc. (Indianapolis, IN) to study the effects of loading rate on effluent water quality, biomass production, and biomass conversion efficiency. Figure 4.1 shows a cross-sectional drawing of the Algaewheel® system and pictures of the experimental setup. Two parallel Algaewheel® systems were used in this study to provide replicated results. The working volume of each tank was 200 gallons. Influent water was pumped from a swine manure lagoon into the first Algaewheel® chamber and then passed through all 6 chambers in sequence. The air flow rate for each tank is 1.5 to 2 SCFM, which maintained a wheel rotation speed of 1 to 2 rpm.

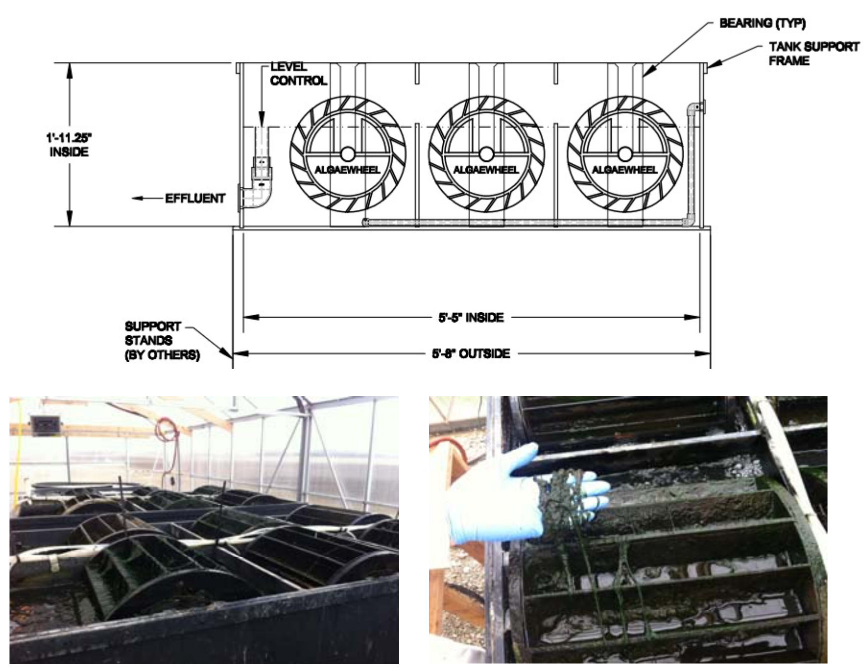


Figure 4.1 Algaewheel® wastewater treatment system layout and operation photos

4.2.2 Harvesting and dewatering methods

It has been reported that decay of biofilm can release nutrients back into water, which reduces water treatment efficiency. Therefore, it is important to regularly remove biomass in the system before decay. In this study, biomass was harvested three times a week. Attached biofilm and filamentous algae were scoured and pulled off from the wheels. Settled biomass were harvested using vacuum. Collected biomass were then dewatered by flat sheet microfiltration membranes. The solid content of the dewatered biomass was generally 8~12%. Dewatered biomass were weighed and then stored in a refrigerator for further analysis.

4.2.3 Water quality and biomass analysis

Water samples were first filtered using 0.45μm pore size syringe filters (Whatman Puradisc-25mm) to remove cells and particles. Then, soluble chemical oxygen demand (SCOD) was determined by visible light absorbance after dichromate digestion according to standard methods (Clesceri et al. 1999) with a HACH Model DR/2010 spectrophotometer. Total soluble nitrogen was measured using the HACH TNT Persulfate Digestion Method No. 10072. Ammonia nitrogen was determined according to HACH Nessler Method No. 8038.

4.2.4 Heterotrophic and autotrophic biomass estimation

Theoretical heterotrophic biomass production was calculated based on COD reduction using stoichiometric methods, and the biomass yield per gram of organic used will be calculated using the equation below (Wang et al., 2009):

$$\mathrm{C_{10}H_{19}O_3N + 4.375O_2 + 0.625\ NH_3 \rightarrow 1.625C_5H_7O_2N + 1.875CO_2 + 4.75H_2O}$$

$$Y_{biomass/organic} = \frac{\Delta(\mathrm{C_5H_7O_2N})}{\Delta(\mathrm{C_{10}H_{19}O_3N})} = \frac{1.625\ (113\,\frac{g}{mole})}{(201\,\frac{g}{mole})} = 0.91\ \frac{g\ cell\ produced}{g\ organic\ used}$$

Then, we calculated the biomass yield per gram of COD as follows:

$$C_{10}H_{19}O_3N + 14.75O_2 \rightarrow 10CO_2 + 9.5H_2O + NO_3^-$$

$$f_{COD} = \frac{\Delta(O_2)}{\Delta(C_{10}H_{19}O_3N)} = \frac{14.75(32\frac{g}{mole})}{(201\frac{g}{mole})} = 2.348\ \frac{g\ O_2\ needed\ (COD)}{g\ organic\ digested}$$

$$Y_{biomass/COD} = \frac{Y_{biomass/COD}}{f_{COD}} = \frac{0.91\ (\frac{g\ cell\ produced}{g\ organic\ used})}{2.348\ (\frac{g\ COD}{g\ organic\ digested})} = 0.39\ \frac{g\ cell\ produced}{g\ COD}$$

The autotrophic biomass is calculated based on the subtraction of theoretical heterotrophic biomass from the total harvested biomass as follows.

$$Y_{auto} = Y_{Total} - Y_{hetero}$$

Autotrophic biomass included both photoautotroph and chemoautotroph biomass. The major community of chemoautotrophs is nitrifying organisms, which can obtain energy from oxidizing ammonia (Nitrosomonas) and nitrite (Nitrobacter). The biomass yield of nitrifiers can be calculated by the following equation:

$$55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_5H_7NO_2 + 54NO_2^- + 57H_2O + 104H_2CO_3 \quad \text{(Nitrosomonas)}$$

$$44NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7NO_2 + 3H_2O + 400NO_3^- \quad \text{(Nitrobacter)}$$

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7NO_2 + 0.98NO_3^- + 1.041H_2O + 1.88H_2CO_3 \quad \text{(Total)}$$

$$Y_{nitrifier/NH4} = \frac{\Delta\ (C_5H_7NO_2)}{\Delta\ (NH_4 - N)} = \frac{0.021(113\frac{g}{mole})}{(14\ \frac{g}{mole})} = 0.16\ \frac{g\ cell\ produced}{g\ NH_4 - N\ oxidized}$$

Finally, photoautotroph productivity can be calculated as:

$$Y_{photoauto} = Y_{Total} - Y_{hetero} - Y_{nitrifier}$$

4.2.5 Hydrothermal liquefaction

Algal biomass harvested from the Algaewheel® were dewatered to a moisture content of 80% and then subjected to HTL conditions (300 ºC, 10-12 MPa) with a reaction time of 30 min to test the feasibility of converting them into bio- crude oil. The HTL experiments were performed according to previously reported methods (Yu et al. 2011) using a 100 ml completely mixed stainless steel reactor with a 70 ml operating volume. The HTL product mixture was separated using a vacuum filter (Whatman No. 4 Filter Paper) into a water insoluble product and PHWW. Moisture content of the water insoluble product was determined by distillation according to ASTM Standard D95-99 (ASTM 2004a). Raw oil was then defined as the water insoluble product after moisture removal and includes both oil and residual solids. The residual solids fraction in the raw oil product was measured as the toluene insoluble portion after a Soxhlet extraction according to ASTM Standards D473-02 (ASTM 2004b) and D4072-98 (ASTM 2004c). The toluene soluble fraction is referred to as bio-crude oil. HHV (kJ/kg) is the higher heating value of the bio-crude oil, and it was calculated according to the Dulong formula (Brown et al. 2010; Zhou et al. 2010).

$$HHV(MJ \cdot kg^{-1}) = 0.3383 \cdot C + 1.422(H - \frac{O}{8})$$

4.3 Results and Discussion

4.3.1 Effects of loading rate on water quality

Table 4-1 shows the effluent water quality and nutrient removal for the Algaewheel® system operated at different HRTs, which are inversely related to the loading rate of organics and nutrients to the system.

Table 4-1 Summary of steady-state removal of priority pollutants at different HRT

	HRT		
	1 day	2 day	4 day
Average light intensity (W/m^2)	68± 12.4	69± 9.4	96± 10.4
Average water temperature (°C)	11.2± 3.4	15.6± 3.8	21.4± 4.6
Average pH	7.45± 0.83	7.73± 0.77	7.88± 0.75
Effluent water quality (mg/L)			
SCOD	121.31± 5.72	117.00± 7.85	109.90± 13.46
TDN	232.5± 32.1	261.5± 12.7	218.1± 25.1
NH3-N	1.09± 0.28	1.42± 0.26	1.77± 0.88
NO2-N	2.38± 0.22	1.41± 0.12	0.41± 0.29
NO3-N	198.9± 15.7	242.0± 12.8	216.2± 29.4
TDP	4.39± 0.80	3.50± 1.42	0.49± 0.37
Pollutant removal percentage (%)			
SCOD	45.8± 3.5%	46.7± 3.2%	42.0± 3.7%
TDN	3.6± 4.8%	4.9± 4.2%	10.7± 6.4%
NH3-N	98.6± 0.5%	98.0± 0.8%	98.3± 1.0%
NO2-N	-	-	-
NO3-N	-	-	-
TDP	11.4± 7.8%	29.9± 6.8%	89.1± 8.2%
Pollutant removal rate (g/m^2-d)			
SCOD	51.9± 6.9	26.0± 2.4	10.1± 2.0
TDN	4.3± 5.7	3.42± 3.0	3.3± 2.2
NH3-N	38.2± 12.0	17.8± 2.1	12.6± 1.7
NO2-N	-1.2± 0.1	-0.34± 0.03	-0.04± 0.04
NO3-N	-31.3±10.7	-13.4± 5.6	-10.1± 2.9
TDP	0.4± 0.3	0.4± 0.2	0.5± 0.1

4.3.1.1 SCOD removal

As shown in Table 4-1 and Figure 4.2, the effluent SCOD concentration for an HRT of 1, 2 and 4 days were 121.3 ±5.7, 117.0 ±7.9 and 109.9 ±13.6 mg/L respectively. These results showed that there is no statistically significant difference in effluent SCOD concentration for the various HRT and temperature conditions. This can be explained by the presence of a fairly consistent recalcitrant fraction of the swine wastewater and all the operating conditions reached the limit of removal for biodegradable SCOD. Side-batch tests with extended aerobic conditions showed that only 43 to 54% of the swine wastewater organics from lagoon stabilization pond were biodegradable. Min et al. (2013) identified key organic components in lagoon digested swine wastewater, which suggested that benzene ring structures decomposed from lignin was a major reason for low biodegradability. Since lignin is one of the major components in swine manure, it is not surprising that a high fraction of recalcitrant organics was observed in lagoon digested swine wastewater.

The SCOD removal rate for an HRT of 1, 2 and 4 days were 45.8%, 46.70% and 42.0%. Considering the fact that the effluent SCOD levels for all three HRTs were quite similar and the longest HRT had the lowest level of removal, the differences in SCOD removal rate are most likely due to natural variations of swine wastewater influent. The SCOD removal rate for an HRT of 1 day, 2 day and 4 day were 51.91, 26.02 and 10.07 $g/m^2/d$, respectively. The removal amount is strongly correlated to the organic loading rate (r^2=0.9). A previous study on algal wastewater treatment reported a COD removal rate of 7.21±4.37 $g/m^2/d$ for a 4 day HRT (Min et al., 2013). Our system was able to achieve higher rates of COD removal because of the aeration for wheel rotation provided extra oxygen in addition to the oxygen produced from photosynthesis. Based on typical algal photosynthesis stoichiometry, 1.34 gram of oxygen was generated per gram of algal biomass synthesized (Brune et al. , 2003). For a well operated high-rate algal pond, the average algal biomass productivity is 22 g/m^2-d which equals to 29.5 g oxygen generated in water for organic and ammonia oxidation (Lundquist et al., 2010).

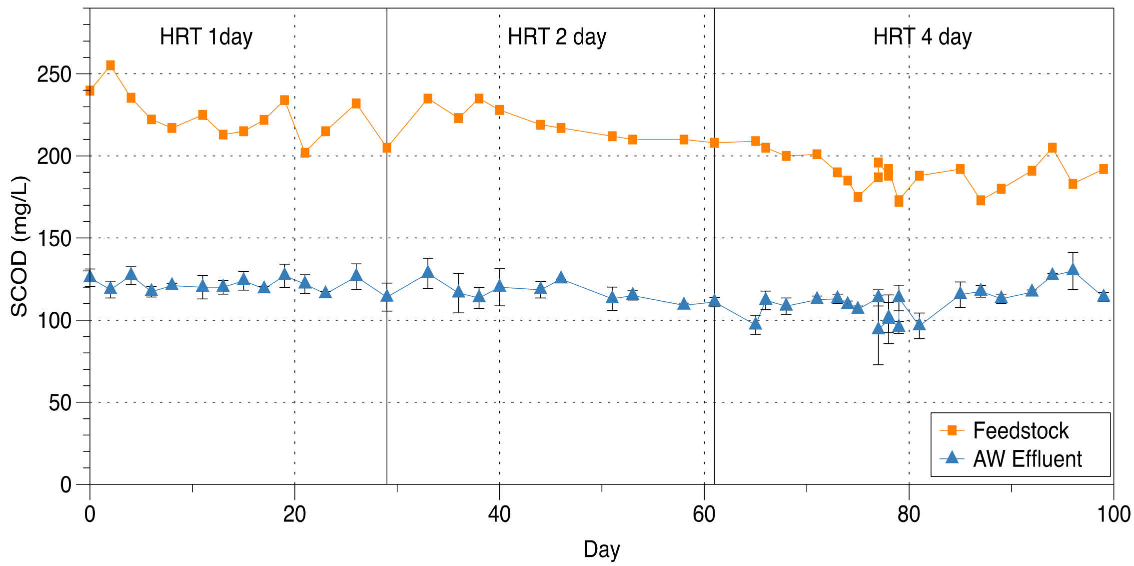


Figure 4.2 Influent and effluent Soluble COD for different HRTs

4.3.1.2 Nitrogen removal

Illinois EPA requires that all water discharged into rivers or lakes contain less than 2.5 mg/L of ammonia nitrogen (IPAC, 2014). As shown in Table 4.1 and Figure 4.3, the effluent ammonia concentration for an HRT of 1 day, 2 day, 4 day were 1.09, 1.42, 1.77 mg/L, respectively, which all met the discharge standard. The TDN removal percentage and removal rate for 1 day, 2 day, 4 day were 3.6%, 4.9% 10.7% and 4.25, 3.42, 3.32 g/m^2-d, respectively. The total nitrogen removal rate is comparable to other similar but slightly less than one previous reported result (4.6 g/m^2-d) in a similar application (Min et al., 2013). Our results showed that the 4 day HRT had the highest TDN removal percentage, but the 1 day HRT had the highest TDN removal rate. TDN included several different forms of nitrogen (ammonia, nitrite, nitrate and organic nitrogen). Because the system was operated aerobically, which limited denitrification and because ammonia volatilization and precipitation is minimal at the neutral pH levels observed in this study (Liao et al., 1993; Nelson et al., 2003), the reduction of TDN was mostly caused by biological assimilation. Figure 4.4 shows the nitrogen profile changes between influent and effluent at different HRT with each N-species having a different y-axis scale focused on its range of values. Our results showed that most of the ammonia were converted into nitrate in the effluent for all three HRTs, which indicates ammonia oxidizing bacteria (AOB) or ammonia oxidizing Achaea (AOA) were the main ammonia removal mechanisms in the system.

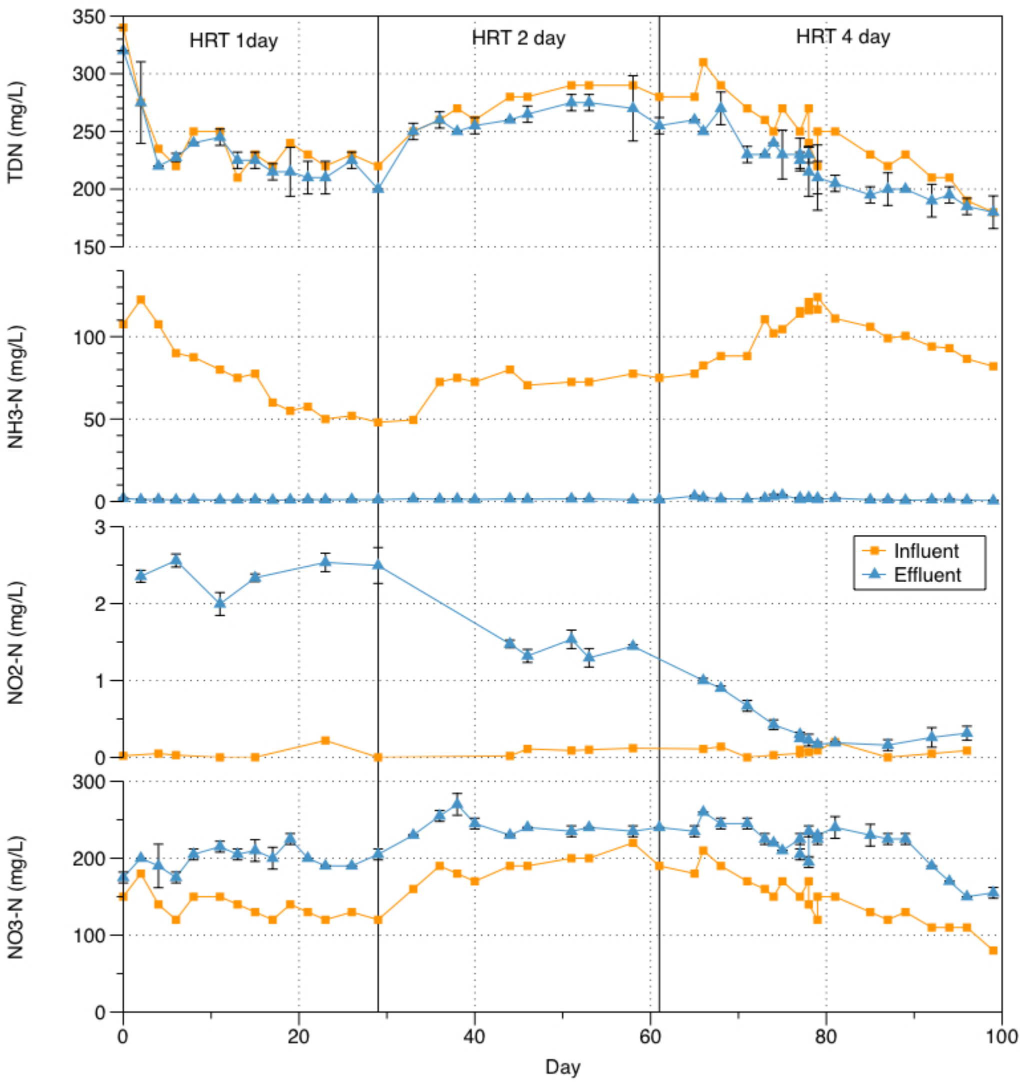


Figure 4.3 Influent and effluent levels of TDN, NH3-N, NO2-N and NO3-N

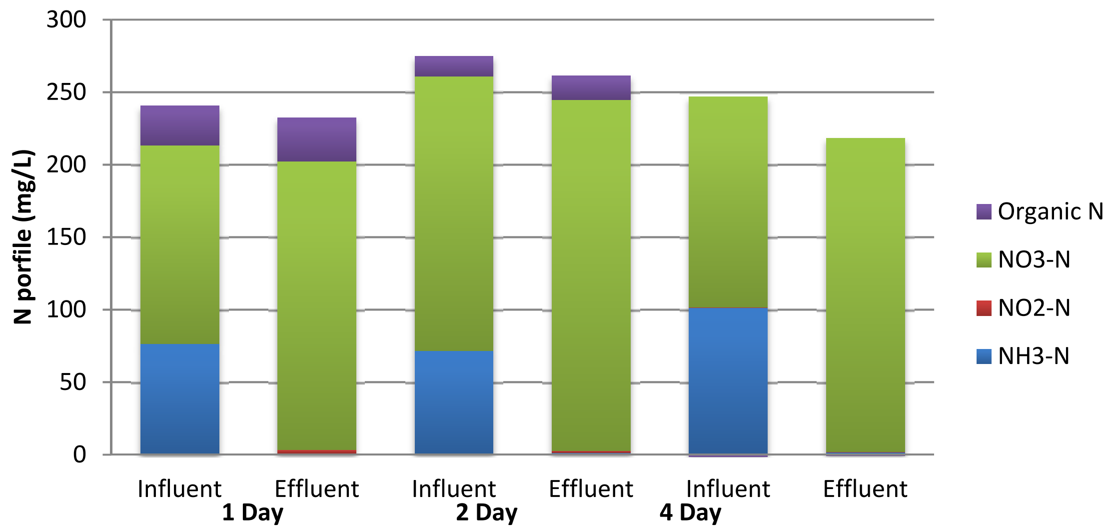


Figure 4.4 Average nitrogen speciation of influent and effluent at different retention time

4.3.1.3 Phosphorus removal

Illinois EPA requires all water discharged into a river or lake to contain less than 1 mg/L of phosphorous as P (IPAC, 2014). Figure 4.5 shows the TDP concentration in the effluent. The effluent total phosphorous concentration at HRT of 1 day, 2 day, 4 day were 4.39, 3.50, 0.49 mg/L, respectively. Thus, only an HRT of 4 days met the phosphorous standard. The TP removal percentage and removal rate for an HRT of 1 day, 2 day and 4 day were 11.4%, 29.9% and 89.1%, 0.29, 0.38 and 0.51 g/m2-d, respectively. The main phosphorous removal mechanisms in wastewater are biological assimilation and chemical precipitation (Larsdotter, 2006; Roeselers et al., 2007). It had been reported that some cyanobacteria are able to accumulate inorganic phosphorus and store it internally as polyphosphates (Kromkamp, 1987). Our results showed a positive correlation of phosphorous removal amount to the autotrophic biomass productivity (r^2=0.93). The autotrophic biomass productivity was highest at an HRT of 4 days, which could be the reason for the higher phosphorous removal.

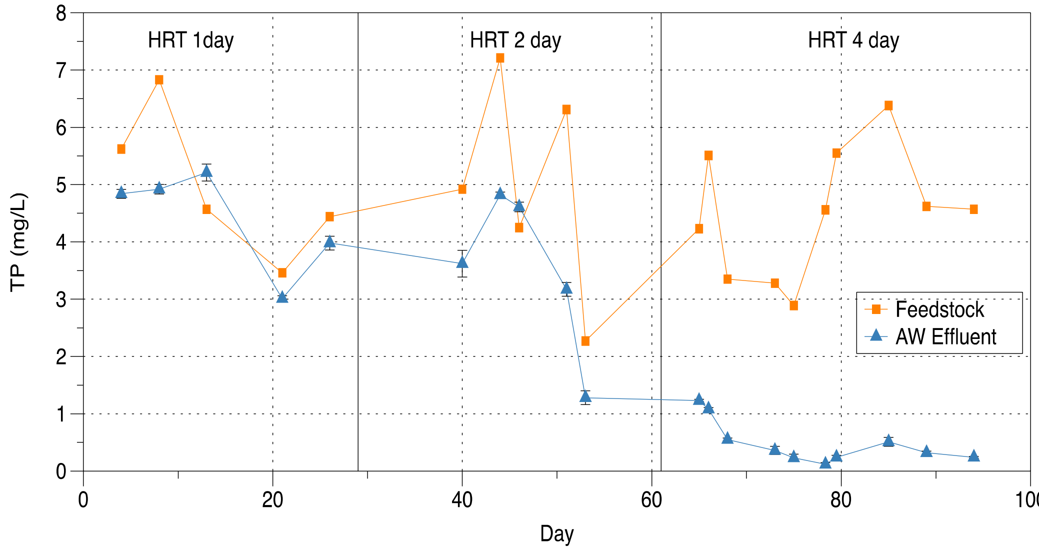


Figure 4.5 Influent and effluent TDP levels for different HRTs

4.3.2 Biomass productivity and characteristics

Table 4-2 shows the biomass productivity of the Algaewheel® system at various HRTs. The total biomass productivity for HRT 1, 2, 4 day were 28.3, 25.3 and 22.3 g/m^2-d, respectively. A 1 day HRT had the highest biomass productivity because of the higher organic and nutrient loading rate. The maximum heterotrophic productivity can be calculated based on the removed organics amount. The results showed the heterotrophic productivity is positively correlated with the organic loading rates. Hence, the 1 day HRT had the highest heterotrophic productivity of 22.0 g/m^2-d, whereas an HRT of 2 days and 4 days was 12.9 and 6.3 g/m^2-d. The chemoautotrophic productivity related to nitrification was calculated based on the ammonia reduction, and the values for 1 day, 2 day and 4 day HRT were 5.0, 2.2 and 1.4 g/m2-d, respectively. By subtracting the heterotrophic and chemoautotrophic productivity from total biomass productivity, the photoautotrophic biomass productivity can be estimated. The estimated autotrophic biomass productivity of HRT of 1 day, 2 day, and 4 day was 1.3, 9.2 and 15.6 g/m2/d, respectively.

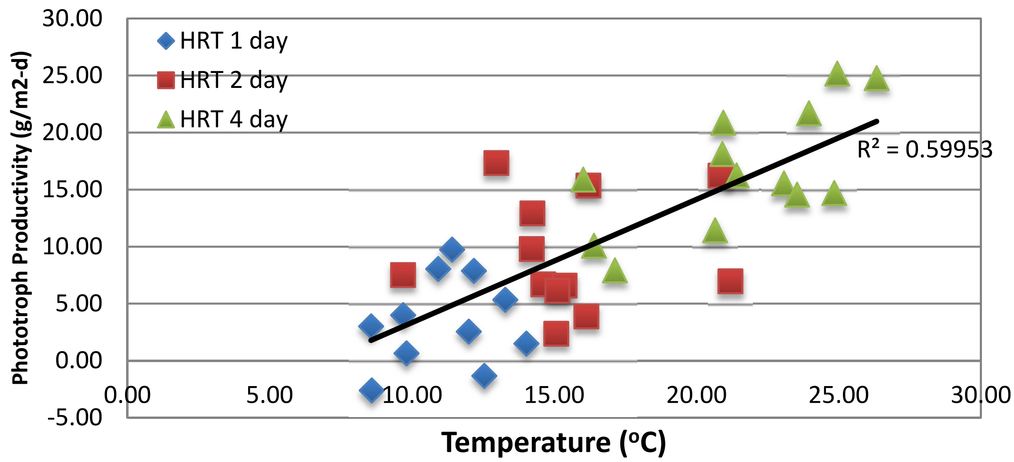
Table 4-2 Biomass productivity and characteritics at different HRT

	HRT		
	1 day	**2 day**	**4 day**
Total Biomass Productivity (g/m^2-d)	28.3	25.3	22.3
Heterotrophic Productivity (g/m^2-d)	22.0	12.9	6.3
Chemoautotrophic Productivity (g/m^2-d)	5.0	2.2	1.4
Photoautotrophic Productivity (g/m^2-d)	1.3	9.2	15.6
Photosynthetic Efficiency (%)	0.4	2.5	3.6
Crude Fat (%VS)	5	4.2	3.1
Crude Protein (%VS)	36.3	39.5	41.2
Carbohydrate (hemi-, cellulose, lignin) (%VS)	58.7	56.3	55.6
Ash Content (%)	32.6±7.3	26.6±9.2	29.1±7.8

The 4 day HRT had the highest photoautotrophic biomass productivity and photosynthetic efficiency due to the combined effects of light, temperature and organic loading. Figure 4.6 shows the effects of temperature and light intensity on photoautotroph productivity at different HRTs for every harvesting event. The fact that photoautotrophic productivities at 3 HRTs have high correlation with temperature (R^2=0.60) suggests that temperature plays a more important role in photoautotroph productivity than loading rate or light intensity. There was a well-established Q_{10} model to describe the response of growth rate to temperature in a light-saturated condition, which is $Q_{10}= (\mu_2/\mu_1)^{10/(\theta_2-\theta_1)}$, where μ_2 and μ_1 are growth rates at temperatures of θ_2 and θ_1, respectively. Many aquatic microorganisms follow this model with a Q_{10} value between 2 and 3. Assuming the algae strains used in this study follow this model, a 5 °C temperature drop would decrease the growth rate 1.41–1.73 times.

The crude fat content of all biomass harvested from the Algaewheel® system were fairly low (<5%). It has been reported that fast-growing algae generally have less lipid content because algae produce and store lipids as the metabolic rate slows down (Williams and Laurens, 2010). Other researchers have also observed the similar relationship (Mata et al., 2010). The crude fat content for biomass produced with an HRT of 1 day was higher than for a 4 day HRT. This may be due to heterotrophic and mixotrophic algae having a higher lipid content than autotrophic algae (Ummalyma and Sukumaran, 2014). Li et al. (2014) studied the effect of autotrophic and mixotrophic growth conditions on lipid productivity of Chodatella sp and showed 5.6 times more lipid productivity for mixtotrophic growth conditions than for autotrophic conditions.

The ash content of the biomass harvested from the Algaewheel® system were higher than other literature reported values for algae. This might be because the swine wastewater has a higher metal and salt content than the municipal wastewater used in other studies, which would end up increasing ash content of wet biomass samples. Higher ash content in biomass is generally considered unfavorable for bio-energy conversion efficiency.



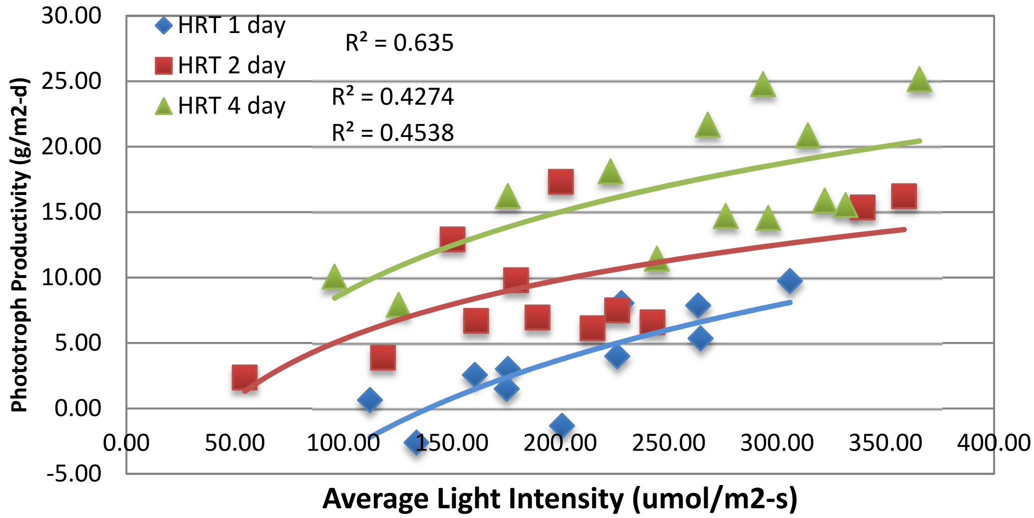


Figure 4.6 Effects of temperature and light intensity on photoautotroph productivity at different HRT

4.3.3 HTL crude oil yield

As shown in Table 4-3, the HHV of biomass harvested at 1 day, 2 day and 4 day HRT is 17, 16.2 and 16.6 MJ/kg, respectively. The biocrude oil conversion ratio for 1 day, 2 day and 4 day HRT biomass is 39.8, 35.2 and 32.7%, respectively. The energy production of 1 day, 2 day and 4 day HRT was 371.7, 293.9 and 245.7 MJ/m^2-d, which suggests the lower HRT is favorable for energy production system. Since temperature is the major factor affecting the biomass production for the system, it is expected to have higher energy yield when operating the system at higher temperatures with a 1 day HRT.

Table 4-3 Biomass HHV and HTL biocrude oil energy production

	HRT		
	1 day	**2 day**	**4 day**
Total Biomass Productivity (g/m^2-d)	28.3	25.3	22.3
C (%)	43.0±1.8	44.1±1.6	45.1±1.1
H (%)	6.5±0.2	6.3±0.13	6.2±0.2
N (%)	6.7±0.03	6.7±0.04	6.0±0.1
O (%)	41.8±2.1	43.0±1.7	42.6±1.4
Biomass HHV (MJ/kg)	17	16.2	16.6
Biocrude Oil Conversion ratio (%VS)	39.8%	35.2%	32.7%
Biocrude Oil HHV (MJ/kg)	33	33	33.7
Energy Production (MJ/m^2-d)	371.7	293.9	245.7

4.4 Conclusions

Wastewater-based microalga biomass production system is considered as one of the most promising approaches for algal biofuel production due to its economic and environmental viability. In this study, a rotating attached growth algal wastewater treatment system was evaluated under different HRT. The areal productivity of ash- free dry biomass ranged from 22 to 28.2 g/m^2-day, which were comparable or higher than the reported productivities derived from a similar research using swine manure. The nutrient removal efficiency was proportional to the biomass productivity. The system was able to meet effluent discharge standard for COD and ammonia even at 1 day HRT. Only the system operated at 4 day HRT met the phosphorus concentration limit for effluent water. In terms of energy production, 1 day HRT had the highest areal energy productivity of 371.7 MJ/m^2-d even though it was operated at a colder time of the year. Although many barriers exist, microalgae have considerable potential to improve the environmental impact of wastewater facilities and support the beneficial reuse of wastewater. More research should be carried out to improve such a system.

5 PILOT-SCALE OPERATION OF ADSORBENTS INTEGRATED BIOFILM ALGAL WASTEWATER TREATMENT SYSTEM AND BIOFUEL PRODUCTION

5.1 Introduction

Combining algae cultivation with wastewater treatment facilities has been highlighted as a promising alternative in recent studies. These studies suggest that algae cultivated in wastewater is one of the best approaches to facilitate biofuels that are both cost-competitive and achieve net environmental benefits (Lundquist et al., 2010; Clarens et al., 2010). The National Algal Biofuels Roadmap has also highlighted several key advantages for integrating algal cultivation with wastewater treatment, such as better water sustainability, low-cost nutrient inputs, and lower net costs for biomass production by using wastewater infrastructure (DOE, 2010). However, growing algal biomass in wastewater can be challenging because of increased potential for contamination and increased complexity associated with simultaneously maintaining effluent water quality goals. Many researches had reported wastewater grown algae had lower lipid content compared to algae grown in synthetic medium (Y. Guo, 2012; Zhou et al., 2013). Therefore, the typical algae biodiesel route is not suitable for wastewater grown algae. Zhou et al. (2013) reported on the so-called environment-enhancing energy process (E2-Energy) that synergistically combines algal wastewater treatment and hydrothermal liquefaction (HTL) for algal biocrude oil production with multi-cycle reuse of nutrients to amplify biomass production. HTL is able to convert low lipid algal biomass into biocrude oil and retain more than 80% of nutrients in post-HTL wastewater (PHWW). Biller et al. (2013) and Zhou et al. (2013) studied the characteristics of the PHWW and tested the ability of algae to grow with different dilution ratios of PHWW. These studies showed although algae can grow on PHWW, significant dilution (50 to 500 times) was required because of toxic compounds such as phenols and nickel presented in PHWW. Dilution is only a desirable alternative when other wastewater streams are available and fresh water is not required. In any case, other alternatives that allow use of less dilution water or none at all when growing algae in PHWW would be highly advantageous.

Elliot et al. (2013) proposed catalytic hydrothermal gasification (CHG) to be an effective process for removing organics in PHWW. They reported the COD in PHWW was 98.8 to 99% removed after CHG, and this allows the nutrients to be recycled back to algae cultivation system. However, Jones et al. (2014) studied the economics of whole algae HTL process including CHG as a wastewater treatment method and estimated the cost of adding CHG to be as high as $1.54 per gallon of oil produced, which was the largest unit process cost. Therefore, there is a need to develop an alternative methods that can effectively reduce the toxicity of PHWW at lower cost.

The goal of this study was to investigate the long-term influence of adsorbents on algal biomass productivity and wastewater treatment efficiency when recycling PHWW and evaluate the feasibility of integrating adsorbents into an algal wastewater treatment system as an alternative for PHWW treatment. This study compared the wastewater treatment performance of the Algaewheel® system with and without adsorbents under conditions or continuous PHWW feeding and with intermittent spike loading of PHWW. The biochemical characteristics of biomass and the yield of HTL biocrude oil were also determined. The performance of adsorbents after extended periods of use were also investigated. The results of this study provide a viable alternative approach for recycling nutrients in PHWW for algal cultivation.

5.2 Material and Methods

5.2.1 Algae cultivation system

The Algaewheel® system developed by OneWater Inc (IN) was used for algae cultivation in this study. As shown in Figure 5.1, the dimension of one Algaewheel® tank is 5’5” x 3’5” x 1’11” (LxWxH) and the working volume is 150 gallon. Each tank contains 6 wheels that were installed in 6 individual chambers. Each chamber is connected in sequence, and thus, influent will flow through all 6 chambers and be sequentially treated by all wheels. Two parallel systems were used in this study to provide the control system (Algaewheel® system without adsorbents) and an experimental system (adsorbent-loaded Algaewheel® system). Each wheel has a coarse-bubble aeration port that provides air for wheel rotation. The air flow rate for each tank is 1.5 to 2 SCFM, which maintained a wheel rotation speed of 1 to 2 rpm.

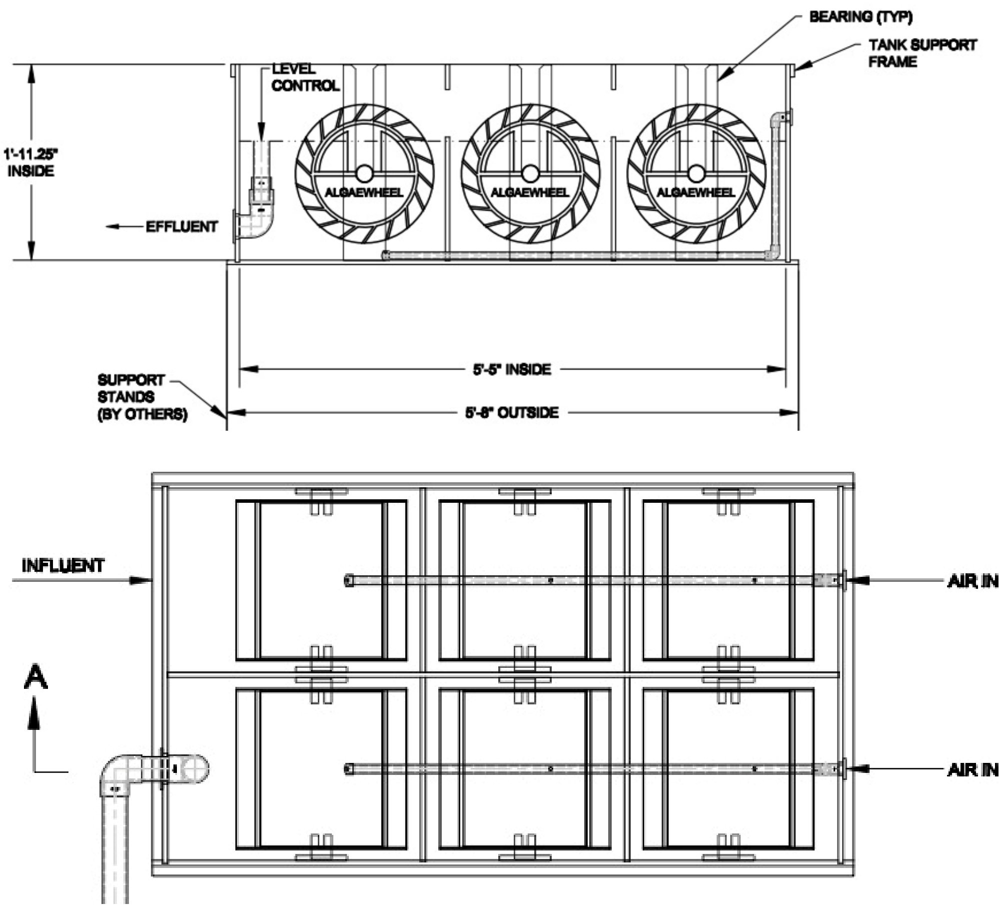


Figure 5.1 Algaewheel® system diagram

5.2.2 Operation condition

There were three operational phases in this study: startup, PHWW spike test and PHWW continuous test. The goals of the startup condition were 1. Allow both systems reach similar condition before adsorbent addition; 2. Study the effects of fresh adsorbent addition; and 3. Confirm there are no outside factors besides the adsorbents that were affecting the experiments by switching wheels between the two systems. Swine wastewater from a storage lagoon were filtered by 200 um filter bag and continuously fed into both systems starting at 4 day HRT and slowly adjusted to 1 day HRT (0.4 LPM) over 1 month. After the system reached steady state, adsorbents were added inside the wheels of one Algaewheel® system. 0.5 kg of extruded activated carbon (EAC) and 0.5 kg of zeolite were mixed together and added inside the first wheel and the second wheel, 1 kg of EAC were added into third and fourth wheel, 1 kg of zeolite were added into fifth and sixth wheel. Wheels were switched between two Algaewheel® tanks to confirm the effects of adsorbents two weeks after the adsorbents were loaded. The order of the adsorbent loaded wheels were also rearranged every week to explore the effects of different adsorbents on pollutant removal.

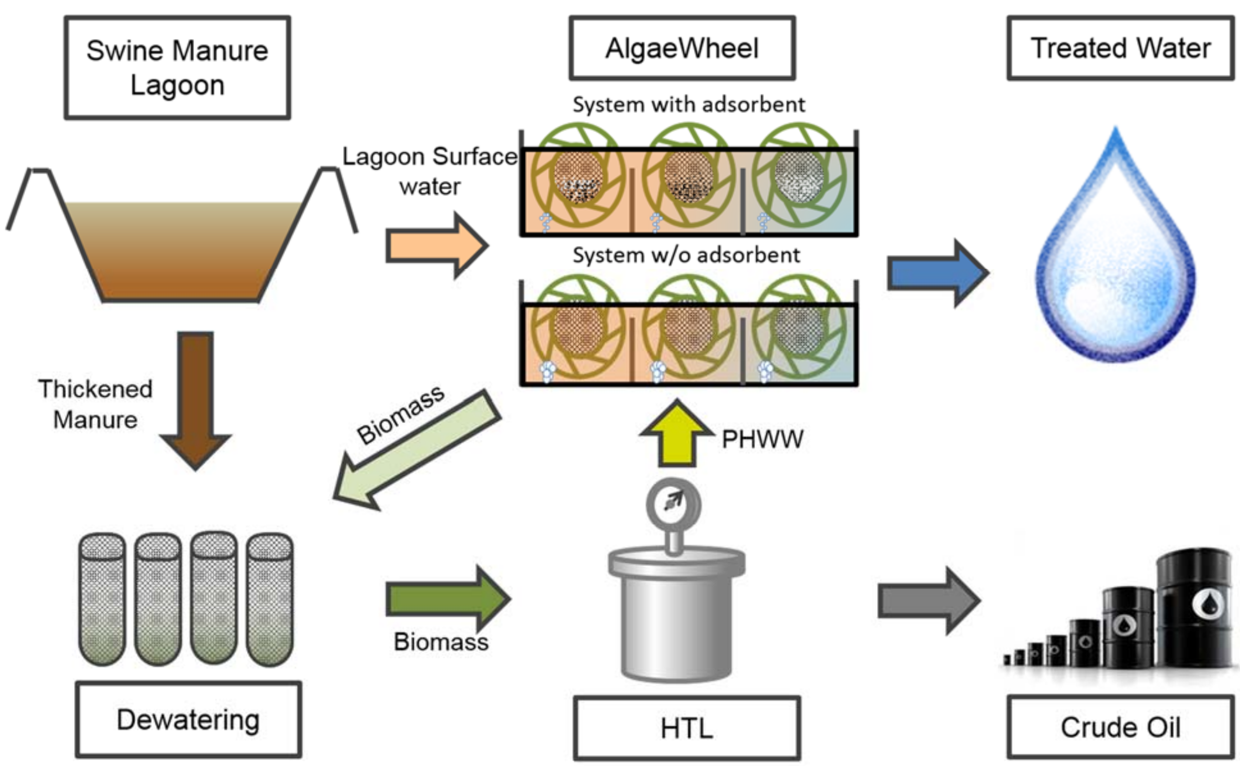


Figure 5.2 System flow diagram

PHWW spike tests were conducted after the system startup phase. The goal of spike testing was to investigate the adsorbent integrated system's stability with variable strength of influent wastewater. PHWW from swine manure was used to represent a high strength wastewater. The characteristics of PHWW are shown in Table 5-1. PHWW was added into the system while the swine wastewater was continuously fed into the system at 1 day HRT. Four PHWW spike concentrations in the first wheel chamber were tested, namely 0.5, 1, 2, and 4%. Water samples were taken at wheels 1, 2, 4, and 6 to track pollutant reduction within the system.

Table 5-1 PHWW water quality

PHWW	
COD	37200±2100
NH3-N	2640 ± 330
pH	7.62 ± 0.29

For PHWW continuous test, a set concentration of PHWW feedstock was premixed in a storage tank and continuously fed both Algaewheel® systems. The concentration of PHWW was stepwise increased from 1% to 1.5% to 2% until the system without adsorbents crashed. Water quality and biomass were measured three times a week. Harvested biomass were saved for HTL.

5.2.3 Biomass harvest and dewatering

Biomass from the Algaewheel® systems were harvested from the clarifiers and the bottom of the tanks by a shop-vac. Each harvesting event removed 50 L of water in the tank. The harvested liquid were then filtered through 100 micron filter bag and sun dried in filter bag for 4 to 24 hours until the solid content was above 10%. Dewatered biomass were then stored in refrigerator for later analysis and HTL.

5.2.4 Adsorbents preparation and analysis

Natural Zeolite NV-Na Ash Meadows Clinoptilolite was obtained from St. Cloud Mine (St. Cloud Zeolite, Winston, NM). The material arrived preprocessed to a standard sieve sizing of 14 x 40 mesh (between 0.4 to 1.4 mm). Before use, the zeolite was rinsed thoroughly with deionized water (DI). For conditioning, zeolite was then soaked in 10% saltwater overnight and rinsed once more with DI water before use. Extruded activated carbon (CalgonCarbon, Pittsburgh, PA) was used for this study. Isotherms for the zeolite and EAC adsorbent were determined by batch testing (Cooney et al. 1998). The designated amounts of adsorbents were put inside the wheels and sealed with 0.5mm opening screen to prevent adsorbent leakage.

5.2.5 Hydrothermal liquefaction

Algal biomass harvested from Algaewheel® were adjusted to a moisture content of 80% and then subjected to HTL conditions (300 ºC, 10-12 MPa) with a reaction time of 30 min to test the feasibility of converting them into bio- crude oil. The HTL experiments were performed according to previously reported methods (Yu et al. 2011) using a 100 ml completely mixed stainless steel reactor with a 70 ml operating volume. The product mixture was separated using a vacuum filter (Whatman No. 4 Filter Paper) into a water insoluble product and PHWW. Moisture content of the water insoluble product was determined by distillation according to ASTM Standard D95-99 (ASTM 2004a). Raw oil was defined as the water insoluble product after moisture removal and includes both oil and residual solids. The residual solids fraction in the raw oil product was measured as the toluene insoluble portion after a Soxhlet extraction according to ASTM Standards D473-02 (ASTM 2004b) and D4072-98 (ASTM 2004c). The toluene soluble fraction is referred to as bio-crude oil. HHV (kJ/kg) is the higher heating value of the bio-crude oil, and it was calculated according to the Dulong formula (Brown et al. 2010; Zhou et al. 2010).

$$HHV(MJ \cdot kg^{-1}) = 0.3383 \cdot C + 1.422(H - \frac{O}{8})$$

5.2.6 Water quality analysis and biomass characterization

Water samples were first filtered using 0.45µm pore size syringe filters (Whatman Puradisc-25mm) to remove cells and particles. Then, soluble chemical oxygen demand (SCOD) was determined by visible light absorbance after dichromate digestion according to standard methods (Clesceri et al. 1999) with a HACH Model DR/2010 spectrophotometer. Ammonia nitrogen was determined according to HACH Nessler Method No. 8038. Biomass biochemical composition were analyzed by Midwest Laboratories which follows AOAC method 903.15, 990.03, 945.16, 942.05 and 973.18.

5.3 Results and Discussion

5.3.1 System startup

The goals of the system startup phase were as follows: (a) to allow both Algaewheel® treatment systems to reach similar operating conditions before adding adsorbents to one system; (b) to study the effects of fresh adsorbent addition; and (c) investigate the effects of different adsorbents on water treatment performance by switching and rearranging wheels between the two systems. Figure 5.3 and Figure 5.4 showed the SCOD and ammonia concentrations in the feedstock and effluent of the Algaewheel® system with and without adsorbents during the startup. Both systems reached steady-state performance by 15 days after the startup. After a period of consistent performance between the two systems, 1 kg of adsorbents were added to the inside of each wheel in one of the systems to observe the effect of adsorbents, while 1 kg of crushed coral was added to each wheel of the other system to compensate for the extra surface area of the adsorbents. After 2 weeks of operation, the wheels were switched between the two systems to verify there was no environmental differences within greenhouse. It was obvious, that after adsorbents were introduced into either system, the effluent water quality improved. The ammonia concentration in the effluent was reduced from 0.65 to 0.28 and from 0.47 to 0.34

mg/L, whereas the COD effluent concentration was reduced from 66.2 to 41.6 and from 57.2 to 37.7 mg/L when the wheels with adsorbents were put into the Algaewheel® System 1 and 2, respectively. During an adsorbent batch pretest, zeolite reached equilibrium status after 4 days. However, the startup results showed that the adsorbents were able to function for over 2 months of continuous usage. This suggests that the adsorbents were adsorbing pollutants and getting in-situ biological regeneration simultaneously.

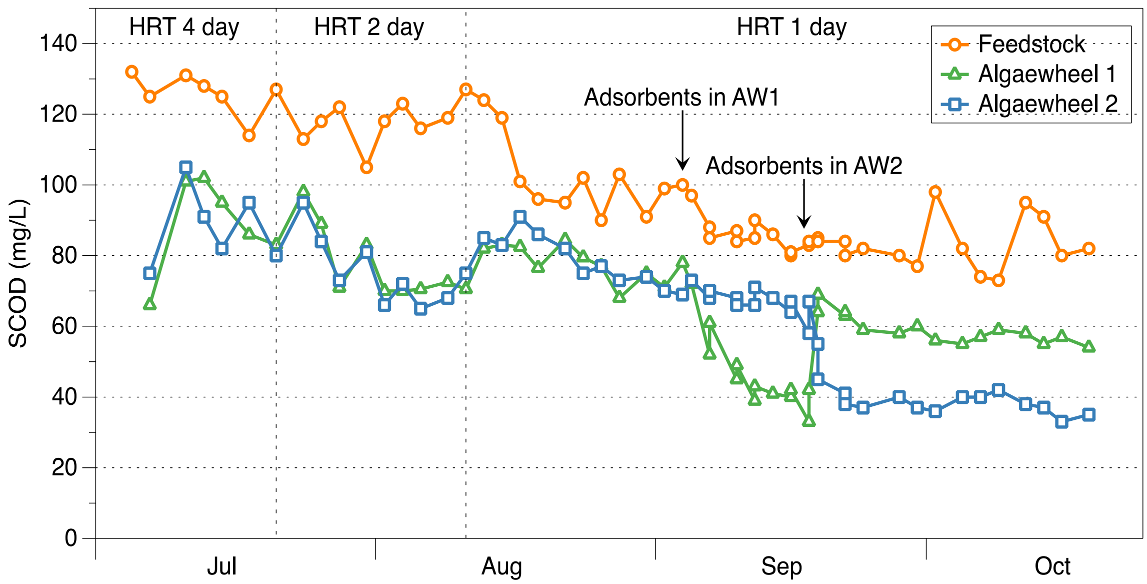


Figure 5.3 SCOD concentration of feedstock and effluent during startup phase

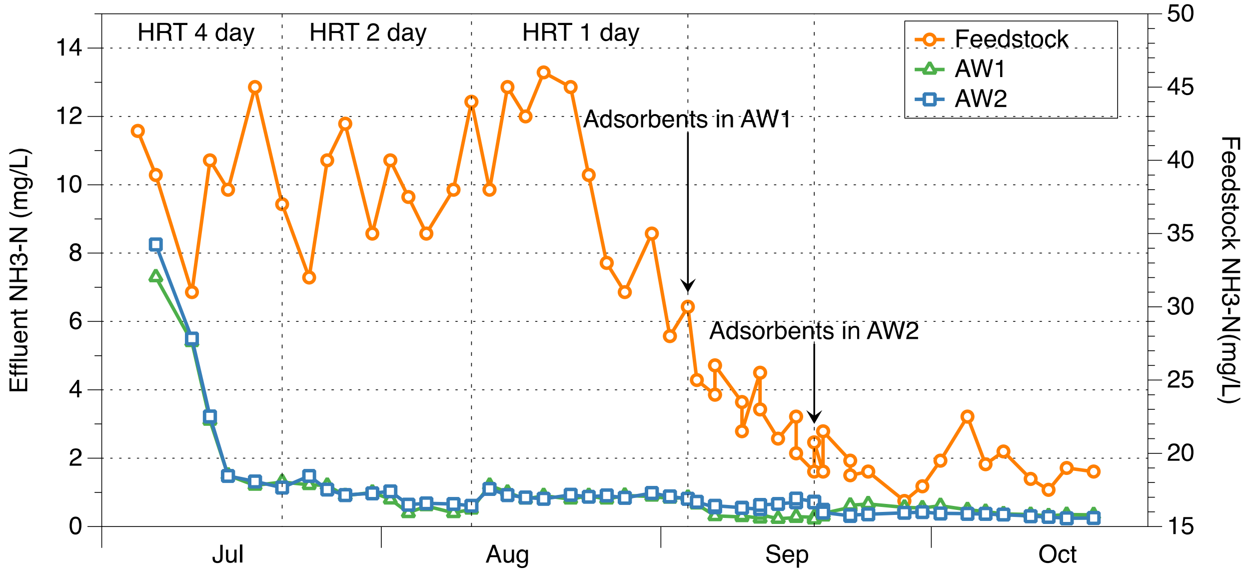


Figure 5.4 Ammonia concentration of feedstock and effluent during startup phase

In order to study the effect of adsorbents on pollutant removal, the water quality of the influent and effluent of each wheel were measured. Figure 5.5 shows the nutrient removal versus the influent ammonia concentration of each wheel with different adsorbents. The results showed that 1 kg of zeolite and mixed adsorbents (0.5 kg of zeolite and 0.5 kg of activated carbon) had better ammonia nitrogen removal rate than 1 kg of activated carbon and wheels without adsorbent. This result agreed with previous batch adsorbents experimental results, in which mixed adsorbents had the highest ammonia removal because the adsorbent mixture provides both the benefits of activated carbon and zeolite.

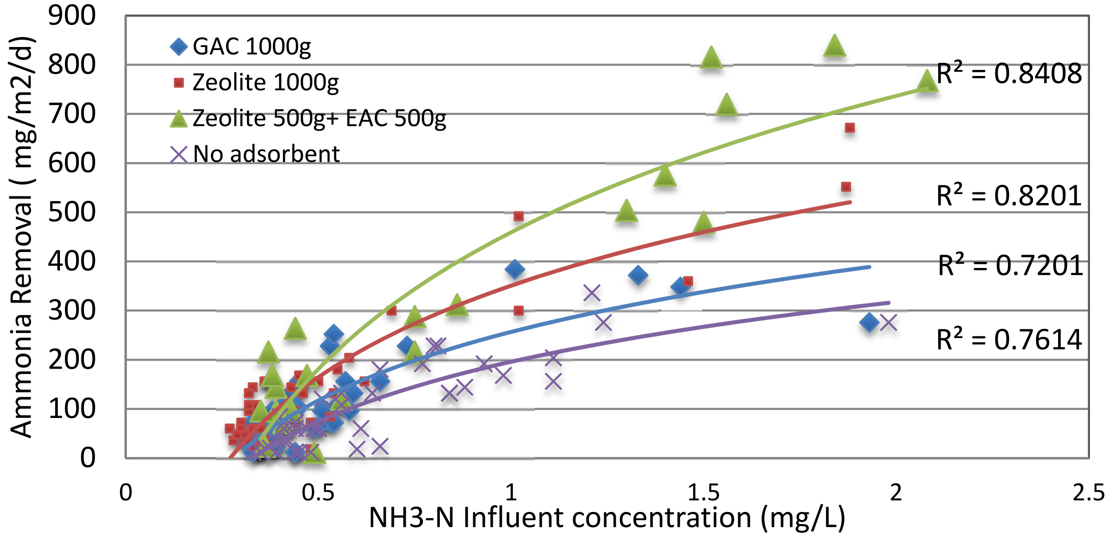


Figure 5.5 Ammonia removal versus influent ammonia concentration for each wheel

Similar phenomenon was also observed for SCOD removal. Figure 5.6 showed the SCOD removal versus influent SCOD concentration. 1 kg of activated carbon and mixed adsorbents had the higher COD removal than 1 kg of zeolite and wheels without adsorbent. These results indicated that a mixture of zeolite and activated carbon had positive interactions that could improve both SCOD and ammonia removal.

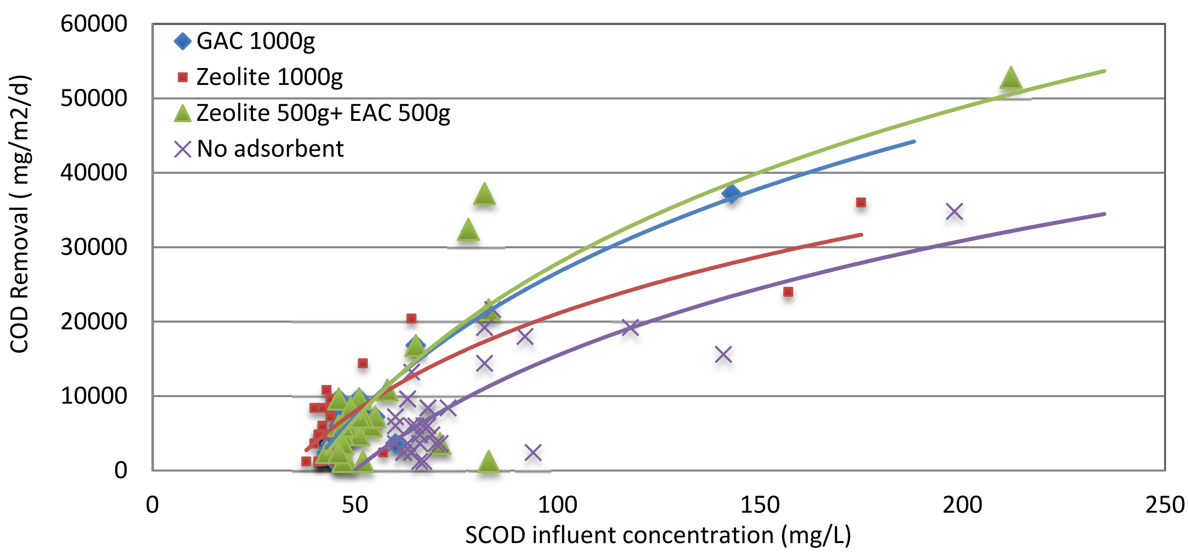


Figure 5.6 SCOD removal versus influent SCOD concentration for each wheel

5.3.2 PHWW spike test

PHWW spiking tests allowed us to study the system responses to sudden shock loading and understand the limitations on system performance when treating variable and high strength wastewaters. As shown in Figure 5.7 and Figure 5.8, ammonia nitrogen and COD concentration across Wheels 1, 2, 4, 6 were compared between systems with and without adsorbents under PHWW spikes. During the spike test, both the first and second wheel in one system were loaded with 0.5 kg of extruded activated carbon and 0.5 kg of zeolite. The third and fourth wheels were loaded with 1 kg of extruded activated carbon, while the fifth and sixth wheels were loaded with 1 kg of zeolite. PHWW was poured into the first chamber while the influent swine wastewater was continuously added at the 1 day HRT rate. A total of 0.5, 1, 2 and 4 L of PHWW were added into the wheel, which corresponds to 0.5%, 1%, 2% and 4% of the first chamber volume, respectively. The first samples were collected immediately after the PHWW was poured.

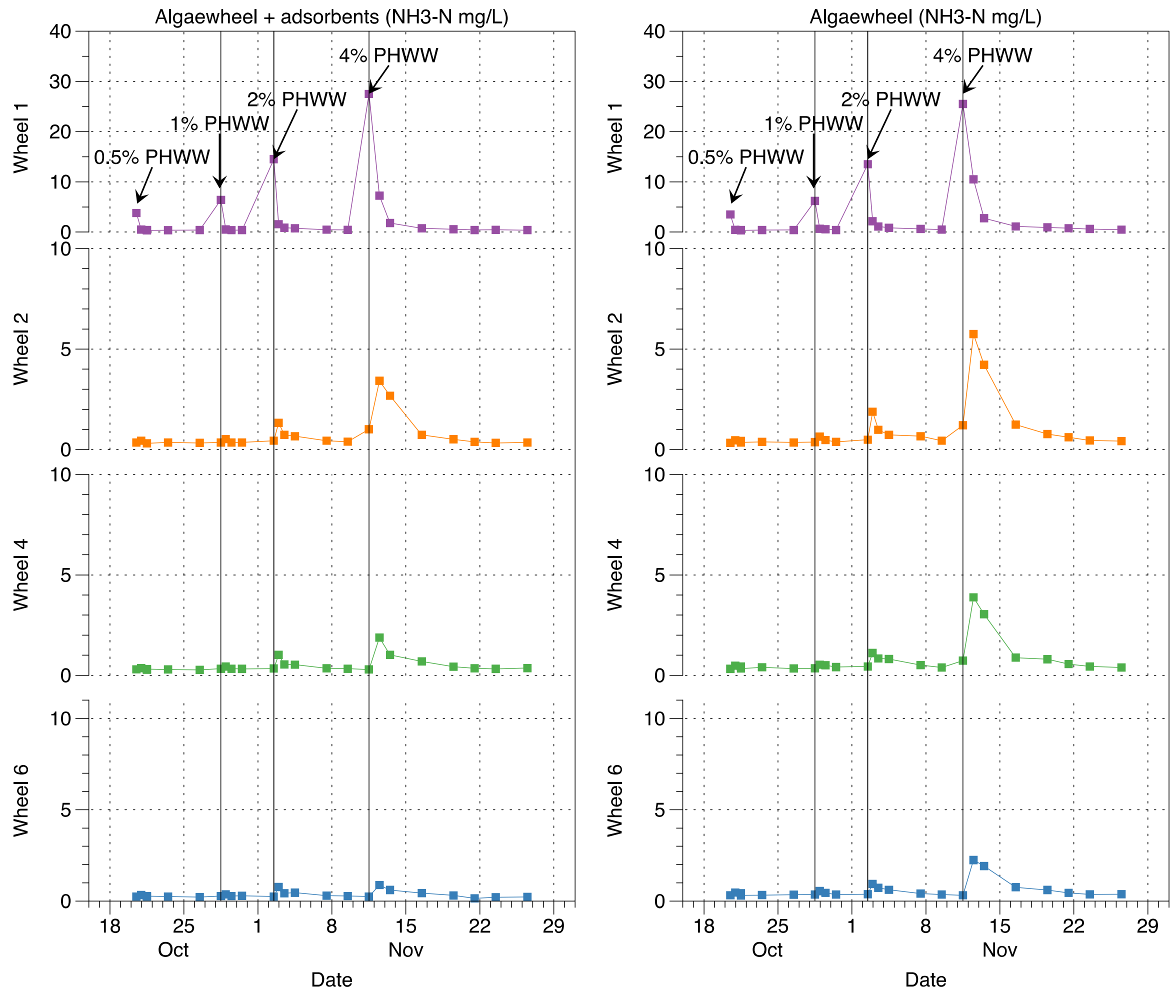


Figure 5.7 Ammonia concentration (mg/L) within chambers during spike test for system with adsorbents (left) and system without adsorbents (right)

The results showed that 0.5 and 1 L of PHWW spike addition had no significant effect on the final effluent water quality (wheel 6). However, the 2 and 4 L spikes had higher ammonia and COD concentrations for the system effluent without adsorbents than the system with adsorbents. This result demonstrated that the system with adsorbents was more capable of retaining nutrients in the system and allowing microorganism to utilize the nutrients. The results also proved that the adsorbent integrated system can maintain effluent quality under aggressive shock loading conditions, which is useful for intermittent discharge operations, including concentrated animal feeding operations.

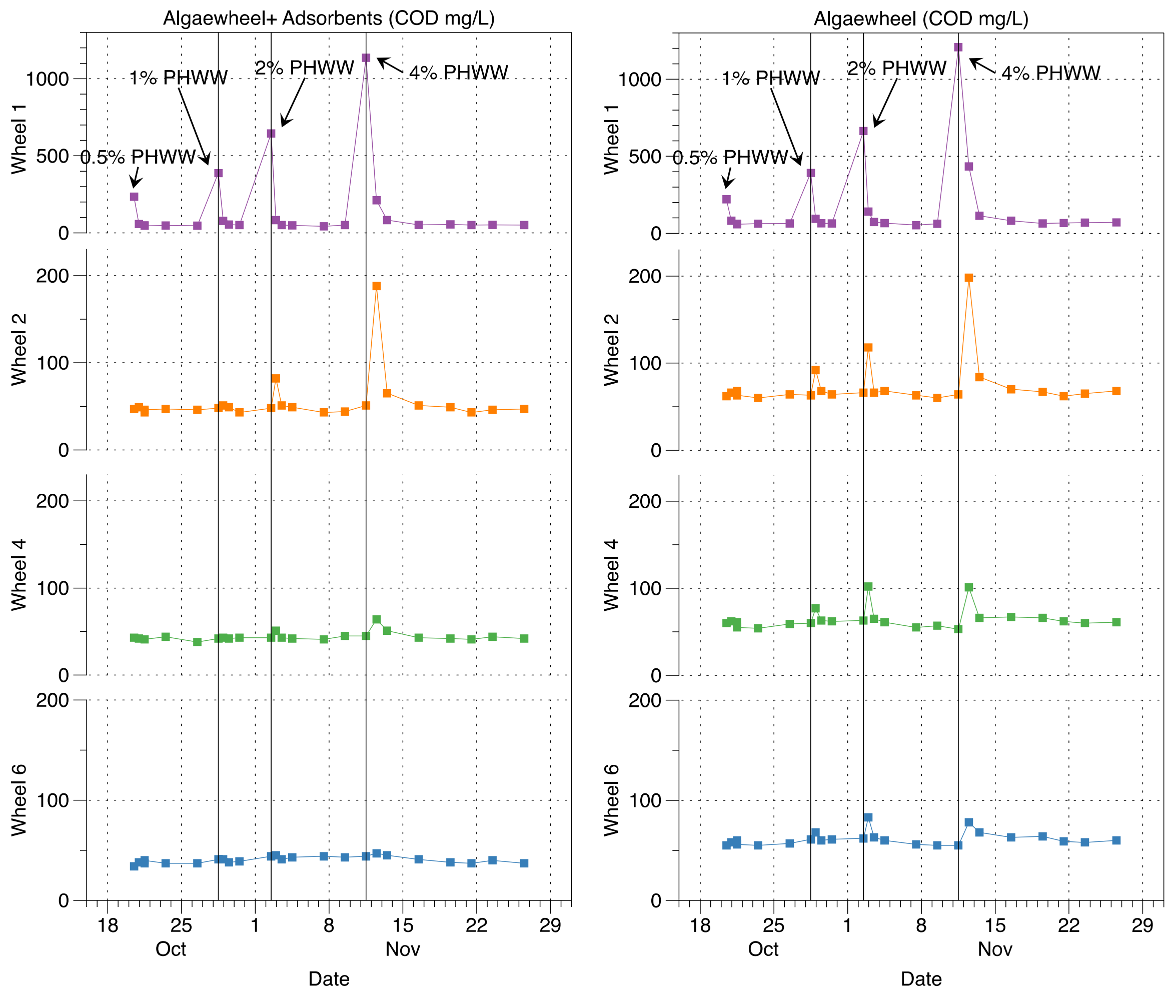


Figure 5.8 SCOD concentration within chambers during spike test for system with adsorbents (left) and system without adsorbents (right)

5.3.3 PHWW continuous addition

5.3.3.1 Water quality for PHWW continuous addition

Figure 5.9 shows the influent and effluent ammonia concentration for system with and without adsorbents when PHWW was continuously added in increasing amounts. The PHWW concentration was increased from 0%, 1%, 1.5% and 2% of PHWW and was blended into a premixed container prior to the system influent. Considering 1 day HRT is much higher flow rate compared to other algae wastewater treatment systems, it was remarkable that both Algaewheel®

systems were able to maintain the effluent ammonia concentration below 1 mg/L even with 1.5% PHWW addition. However when 2% PHWW was added, influent ammonia concentration rose up to 90 mg/L in the system without adsorbents, which lost the ability to remove most of the ammonia. In contrast, the system with adsorbents still able to maintain low ammonia in the effluent. These results demonstrate that the adsorbent integrated system is able to prevent system failure from adding a higher percentages of PHWW continuously.

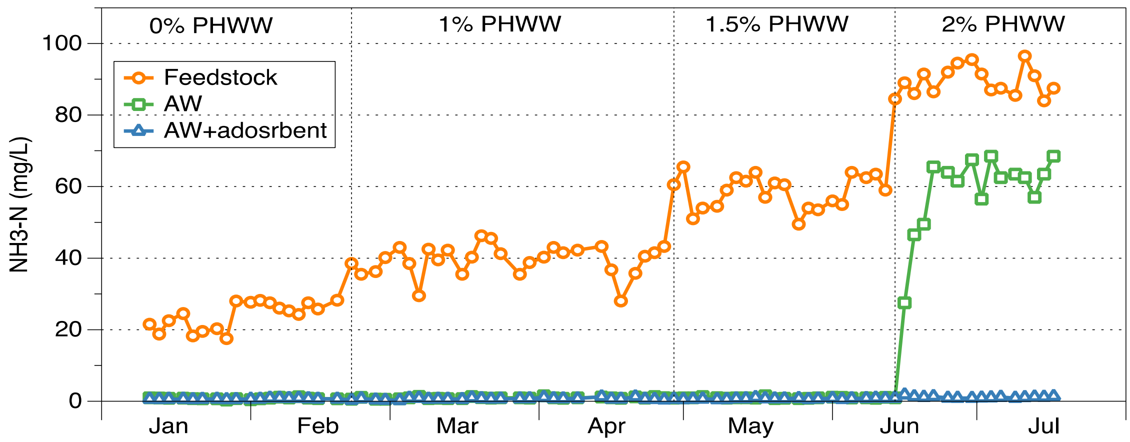


Figure 5.9 Ammonia concentration of feedstock and effluent for Algaewheel® system with and without adsorbents

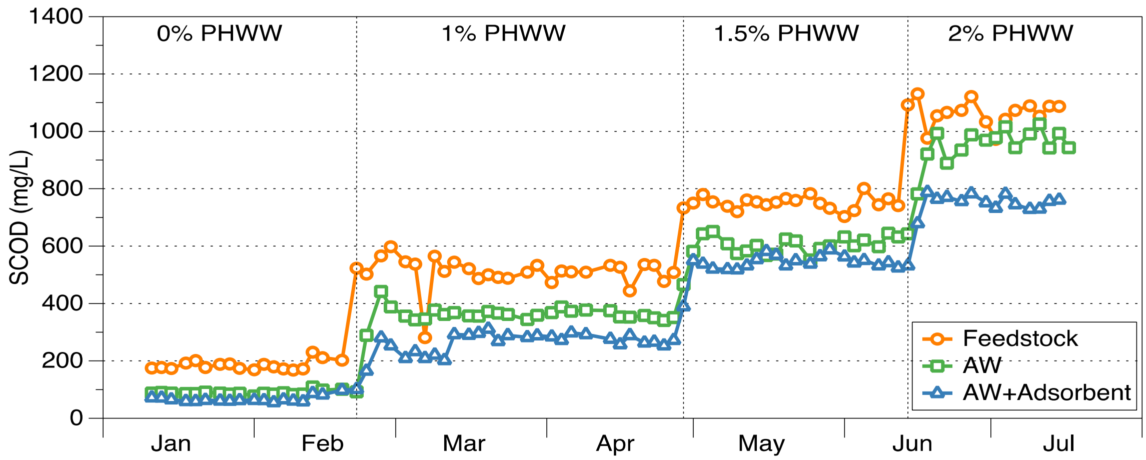


Figure 5.10 SCOD concentration of feedstock and effluent for Algaewheel® system with and without adsorbents

Figure 5.10 showed the influent and effluent soluble COD concentration in the system with and without adsorbents. The system with adsorbents had better COD removal throughout the whole continuous PHWW addition test. The system with adsorbents averaged 13% higher COD removal than the system without adsorbents when PHWW addition was 1.5% or less. The system without adsorbents had a sharp drop-off in COD removal during 2% PHWW addition.

The fact that the system without adsorbents lost most of its ability to remove COD and ammonia with 2% PHWW addition indicates that the system collapsed. It has been reported that PHWW contains some inhibitory compounds (Jena et al., 2010), and Biller et al. (2012) has also studied the effects different dilutions of PHWW on algae growth. He concluded that there is no or very little Spirulina or Chlorella growth on 50X and 100X dilutions due to high concentrations of phenols and heavy metals like nickel. Ammonia toxicity could be another reason for system collapse. Collos and Harrison (2014) had studied the inhibitory and toxic ammonium concentration for different classes of unicellular algae. The results showed Cyanophyceae, Diatomophyceae and Dinophyceae had inhibitory or toxic effects with ammonium concentrations of 90mg/L or less. Other algae have much higher ammonia tolerance, such as Chlorophyceae, which started to have inhibitory effect when ammonium reaches 332 mg/L. Regardless of the relative effects of toxic compounds or ammonia toxicity, this study showed that the Algaewheel® system is capable of removing pollutants when PHWW concentration were below 1.5%, which is higher than other algae cultivation systems reported in the literature. One of the major differences between this study and others is the operating mode. This study is the first research that continuously fed PHWW into the algae cultivation system. Unlike batch operation modes used in previous studies, continuous feeding of PHWW avoids the sudden spike and allows microorganism a better chance to acclimate harsh conditions. However, the fact that microorganism failed to acclimate to 2% PHWW might indicate that the organisms had reached their biological limitation. When adsorbents were present in the system, it can mitigate the toxic effect and maintain good performance at 2% continuous PHWW addition and potentially more.

5.3.3.2 Biomass productivity of PHWW continuous addition test

Figure 5.11 shows the biomass productivity (AFDW) of the two systems with continuous addition of PHWW, and the error bar indicates the standard deviations of total biomass productivity measurements. Biomass were harvested at the bottom of each wheel by vacuum pump every 2 to 3 days. Harvested biomass were then dewatered in 100 micron filter bag until the solids content was above 10%. For the system without adsorbents, it had the highest productivity (28.2 ± 3.62) under 1% PHWW addition then dropped to 21.6± 2.35 and 16.8±2.87 when 1.5% and 2% PHWW added, respectively.

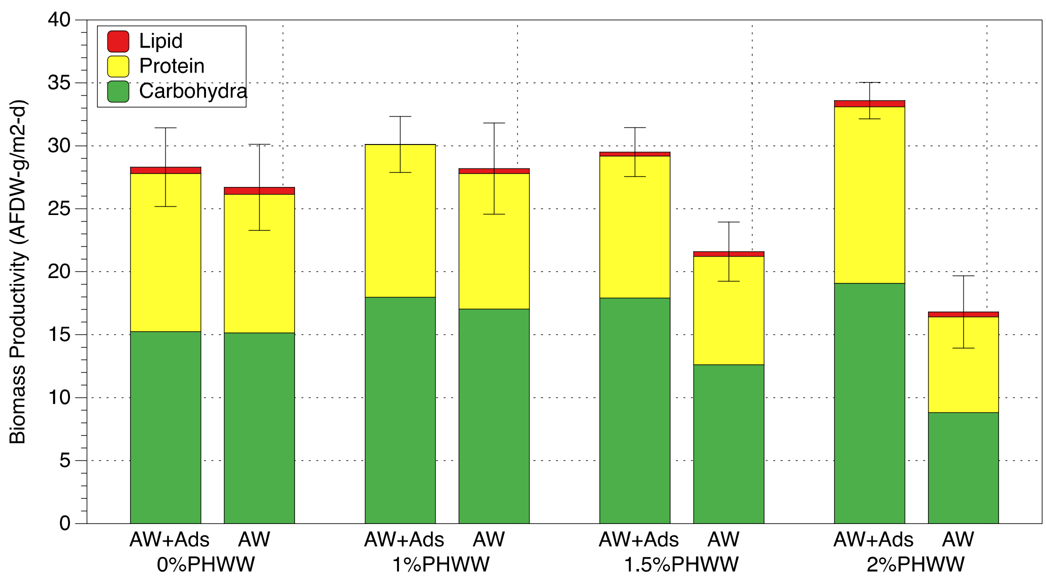


Figure 5.11 Biomass productivity and biochemical composition for Algaewheel® systems under different PHWW blend ratio (error bars present standard deviations of biomass productivity)

Past researches also showed a similar trend. Biller et al. (2012) reported the growth of different algae in 50X to 600X dilutions of PHWW, which showed that Chlorella had the highest biomass growth with 100X PHWW, while Spirulina and Chlorogloeopsis had the highest growth in 400X PHWW. Zhou et al., (2013) also conducted series batch experiments on growing mixed algal-bacterial biomass in 0, 0.5, 1, 2, 5, and 10% of PHWW in municipal wastewater. She reported the biomass production was peaked (541 mg/L) at 0.5% PHWW then significantly dropped to 146 and 101 mg/L at 1% and 2% PHWW. The most reasonable explanation for this trend is that low percentage PHWW addition provided nutrients and organics for algae to grow autotrophic or mixotrophically, and hence, it had higher biomass productivity than the original feedstock. However, when the concentration of PHWW is above certain threshold, the toxic compounds start to inhibit algae growth. In contrast, the biomass productivity in the Algaewheel® system with adsorbents increased as PHWW concentration increased. This result indicates that adsorbents reduced the effective toxicity of PHWW and allowed microorganisms to utilize nutrients in PHWW. It is quite likely that PHWW percentages above 2% would be tolerable with the adsorbent amended Algaewheel® system because productivity was still increasing with 2% PHWW addition, and past studies generally showed a drop off in biomass productivity before organisms were completely inhibited.

5.3.3.3 Ash composition of biomass for PHWW continuous addition test

Figure 5.11 also shows the biochemical macromolecule composition of biomass. There was no significant difference in the biochemical composition between the system with or without adsorbents. There was also no clear trend of biochemical composition change associated with the amount of PHWW added. Biomass harvested in the system were highest in carbohydrates (52.5 to 60.7%), followed by proteins (38.2 to 45.2%), and they were all low in lipids (0 to 2.3%). The biochemical composition of biomass in this study is distinct from the biomass in other wastewater applications. Nielfa et al. (2015) noted the biochemical composition of biological sludge is highest in proteins (58%), followed by carbohydrates (38%) and then lipids (4%).

Michelon et al. (2016) also reported the biochemical compositions of Chlorella polyculture in diluted swine wastewater. In their study, when the polyculture had sufficient N and P, the biochemical composition was low in lipids (less than 3%) and high in proteins (56.1 to 58.9%). When the system had N or P limitations, the carbohydrate content of the biomass increased from 25.2% to 35.3% and 40.4% while lipid content remained below 5%. In our study, carbohydrate is the main compound in the biomass. One possible explanation for high carbohydrate content is that the Algaewheel® system is an attached growth system which forms biofilm rich in extracellular polymeric substance (EPS). EPS can be account for 4 to 9% of total dried sludge and is typically made up of 40 to 95% polysaccharides (Pham 2002). Another possible explanation for high carbohydrate content in the Algaewheel® system is depleted nutrients. During spike tests (Figure 5.7 and Figure 5.8), the nutrients were rapidly taken up in the first two wheels. Thus, the later wheels could be lacking in nutrients. Under N-limited condition, protein synthesis is inhibited and it can trigger carbohydrate formation for energy reserves (Michelon et al., 2016). High carbohydrate content biomass may not be an effective feedstock for biodiesel production, but still could be converted into biofuel through HTL or fermentation.

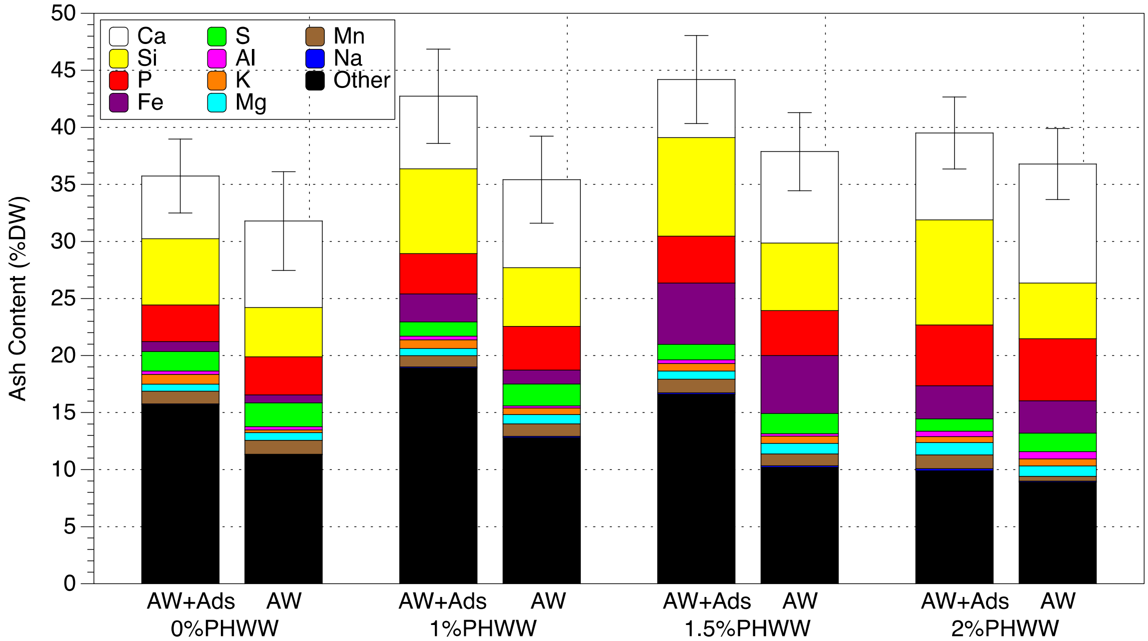


Figure 5.12 Ash content and mineral composition for Algaewheel® systems under different PHWW blend concentration (error bars present the standard deviations of ash contents)

Figure 5.12 shows the ash content and mineral profiles of biomass harvested in both systems under different continuous PHWW concentrations. The error bar shows the range of the standard deviation of total ash content in harvested biomass. As the influent PHWW concentrations increased from 0, 1, 1.5, to 2% The ash content for biomass harvested from Algaewheel® system with adsorbents were 35.7% ± 3.24, 42.7% ± 4.13, 44.2% ± 3.86 and 39.5% ± 3.15 while biomass from Algaewheel® were 31.8% ± 4.33, 35.4% ± 3.81, 37.9% ± 3.42 and 36.8% ± 3.11, respectively. In the literature, the ash content of most of wastewater grown algae are in the range of 3 to 20% depending on the cultivation system and algae species (Zhou et al., 2013). However, some other literature has also observed very high ash content algal biomass. For instance, Kangas and Mulbry (2014) reported the ash content of algal biomass cultivated from agricultural drainage water using algal turf scrubber was 56 to 73%. Hampel (2013) studied the characterization of algae grown on a nutrient removal system installed near

Chesapeake Bay and showed the ash content varied between 32 to 79%. Figure 5.12 also shows that the biomass from the system with adsorbents had 2.7 to 6.3% higher ash content than the biomass from system without adsorbents. Higher ash content could be the result of biogenic minerals forming or extracellular contamination like salt precipitation or potentially could be explained by adsorbent fines leaking out of the wheels.

5.3.3.4 Extracellular ash reduction test

In order to determine the amount of extracellular contamination, 1 mm opening screen was used immediately after harvesting biomass to remove particles such as leaked-out adsorbents. Screened and dewatered biomass was then rinsed by DI water to remove salt or metals that might be adsorbed on cell walls. As shown in Figure 5.13, screening resulted in slightly more ash reduction (2%) for the biomass from the system with adsorbents than the system without adsorbents (0.9%). After rinsing, 3.1% and 2.8% of ash content was reduced for the biomass from system with and without adsorbents, respectively. These biomass treatment results suggested that there was some extracellular contaminations, but this was not the major source of ash. The major ash sources were intercellular minerals.

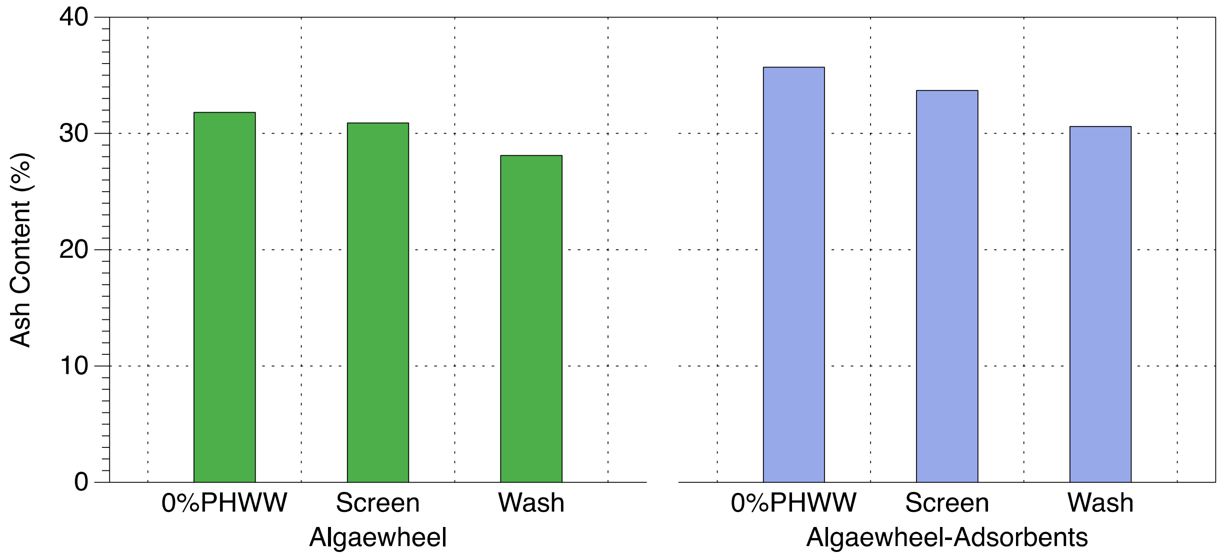


Figure 5.13 Ash content of harvested biomass after pretreatments

Figure 5.12 also shows the mineral profiles of the harvested biomass. 10 different minerals were quantified by ICP-MS and the rest of the ash components like inorganic carbon or oxygen were listed as “Other”. The major minerals in the ash were Ca, Si, P, Fe and S. For the biomass harvested from the system without adsorbents, Ca was the most abundant mineral and followed by Si. Brownlee and Taylor (2002) reported biogenic calcification had direct associations with photosynthesis. Algae species rely on CO_2 diffusion to supply photosynthesis, which may become rate-limited under low CO_2 concentrations. Calcification allows algae to utilize HCO_3^- and produce CO_2 for photosynthesis, and any $CaCO_3$ precipitates formed internal or externally increase the Ca concentration in biomass. For the biomass harvested from the adsorbent integrated system, Si was the most abundant mineral and followed by Ca. It is well known that silicate is the main component in diatom frustules (Brownlee and Taylor, 2002). Fachini et al. (2006) reported zeolite can release silicon into water over time and therefore increase the growth of diatoms.

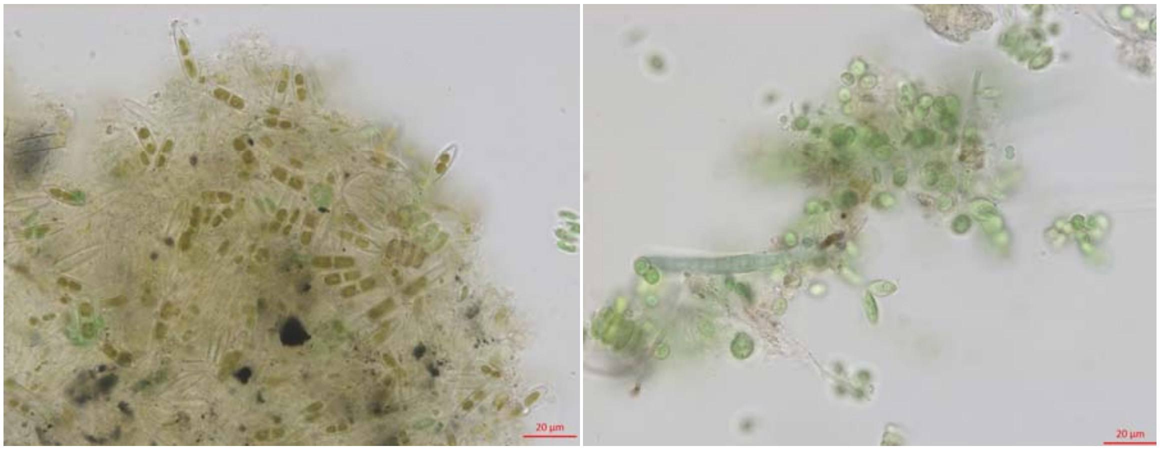


Figure 5.14 Microscopy image of biomass from system with adsorbent (left) and system without adsorbent (right)

Microscope and SEM images (Figure 5.14, Figure 5.15) provided support for the increased proliferation of diatoms in the adsorbent amended system. Based on the cell morphology and numbers of striae on the frustule, the major species present in the adsorbent integrated system was likely to be Nitzschia incospicua (Spaulding et al., 2010). There were more species of algae identified in the system without adsorbents like Scenedesmus sp. and Chlorella sp. Although a more detail species analysis will need to be done in the future, it was clear that the system without adsorbents were mostly green algae.

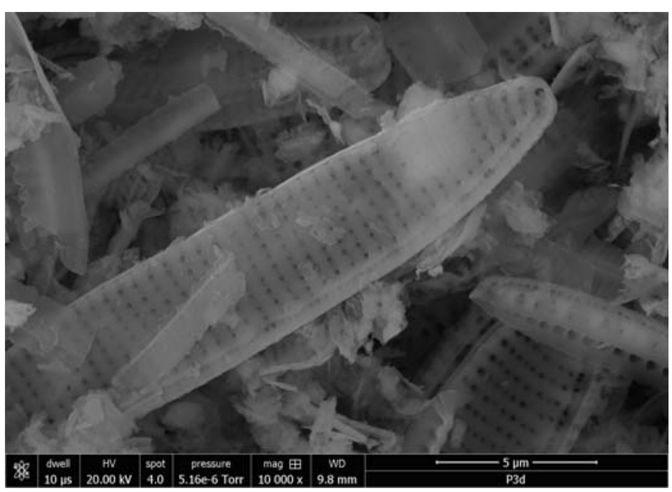


Figure 5.15 SEM image on the harvested biomass

High ash content is known to generally reduce HTL crude oil yield, decrease conversion energy efficiency and might reduce catalyst lifetimes if used (Guo, 2012). Therefore it is important to develop pretreatment processes that can decrease ash content before conversion. For example, dilute acid treatment is effective to remove calcium in biomass.

5.3.3.5 Hydrothermal liquefaction of biomass from PHWW addition test

Table 5-2 HTL results of biomass harvested from Algaewheel® systems

	0% PHWW		1% PHWW		1.5% PHWW		2% PHWW	
	AW	+Ads	AW	+Ads	AW	+Ads	AW	+Ads
Biomass productivity (AFDW g/m2-d)	26.7 ± 3.4	28.3 ± 3.1	28.2 ± 3.6	30.1 ± 2.2	21.6 ± 2.4	29.5 ± 1.9	16.8 ± 2.9	33.6 ± 1.5
Crude Oil Yield (% AFDW)	29.6 ± 2.3	30.4 ± 3.1	27.5 ± 4.2	26.4 ± 2.6	28 ± 2.5	25.9 ± 1.2	29.8 ± 1.8	27.6 ± 3.2
Oil HHV (MJ/kg)	29.8	31.5	28.1	29.6	29.3	27.2	31.9	30.1
Energy Yield (kJ/m2-d)	235.5	271.0	217.9	235.2	177.2	207.8	159.7	279.1

Table 5-2 shows the biocrude oil yield and energy yield for the system with and without adsorbents under different feedstock PHWW concentrations. The biocrude oil yield for the Algaewheel® system with adsorbents were 30.4% ± 3.1, 26.4% ± 2.6, 25.9% ± 1.2 and 27.6% ± 3.2 while the yield for Algaewheel® were 29.6% ± 2.3, 27.5% ± 4.2, 28.0% ± 2.5 and 29.8% ± 1.8 when feedstock PHWW concentration were 0, 1, 1.5, 2% respectively. The results showed the biomass from the system without adsorbents had slightly higher biocrude oil yield than the system with adsorbents. This is likely explained by the higher ash content, which can inhibit biocrude oil formation and deteriorate biocrude oil quality (Chen et al., 2014). In this case, there was no clear effect of the higher ash content on oil quality, which was quantified as HHV. However, the adsorbent integrated system clearly yielded more total energy than the Algaewheel® system without adsorbents because the overall biomass productivity was higher under each different influent condition. Thus, these results showed integration of adsorbents into Algaewheel® system not only enhanced wastewater treatment performance but also increased energy production.

5.3.4 Effects of adsorbent service time

There are always concerns related to the service time of the adsorbents in wastewater treatment applications. The frequency of adsorbent replacement will directly impact the overall system economics, and can make an application infeasible if the frequency is too high. Adsorbents like granular activated carbon typically have a minimum service life of six months in large-scale water purification systems. In order to address these concerns, equilibrium and kinetic experiments were conducted to compare the efficiency of the virgin adsorbents to the adsorbents after 4 months and 10 months of usage.

5.3.4.1 Zeolite equilibrium and kinetic curve

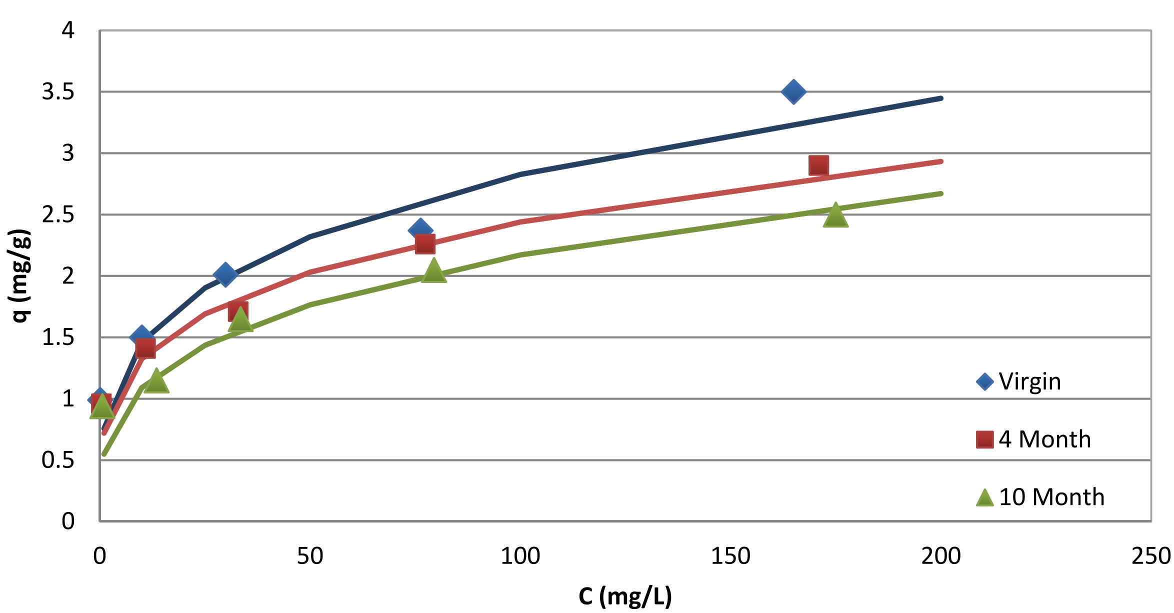


Figure 5.16 Equilibrium curve for zeolite at different service time

Figure 5.16 shows the ammonia equilibrium isotherm data for zeolite after 0, 4 and 10 months of service time. The Freundlich equation was used to describe zeolite adsorption isotherm. Table 5-3 presents the Freundlich equation parameters of adsorption capacity (K) and strength of adsorption (1/n) for the zeolite samples with different service times. These results show that the Freundlich equation was able to fit the zeolite isotherms well ($R^2 > 0.96$). While the 1/n value remained fairly consistent, the adsorption capacity parameter K was reduced from 0.76 to 0.72 and 0.55 after 4 month and 10 months of usage, respectively, which corresponds to a 5.3% and 27.6% capacity reduction. Margeta et al. (2013) reported the ammonium sorption efficiency of zeolite was sharply decreased after 70 hours of usage in column without any regeneration. Comparing the results of this study to the literature, this study indicates that bioregeneration was occuring in the Algaewheel® system because the zeolite with service time of 10 months maintained more than 70% of virgin adsorption capacity.

Table 5-3 Freundlich constants for zeolite at different service time

	Virgin	4 Month	10 Month
K	0.76	0.72	0.55
1/n	0.29	0.27	0.30
R2	0.96	0.98	0.99

Another potential concern with using adsorbents in a wastewater algae cultivation system would be that the biofilm may significantly retard the adsorbate diffusion, and thus decrease the adsorption efficiency. Zeolite kinetic analysis were conducted to address this question. As shown in Figure 5.17, virgin zeolite had faster adsorption rate than 4 month, and 10 month old zeolite. Although the Lagergern pseudo-first-order equation is widely used to describe adsorption kinetics, Kucic et al. (2012) determined the adsorption of ammonium on zeolite is not a first order reaction and proposed a pseudo-second-order equation as zeolite kinetic model.

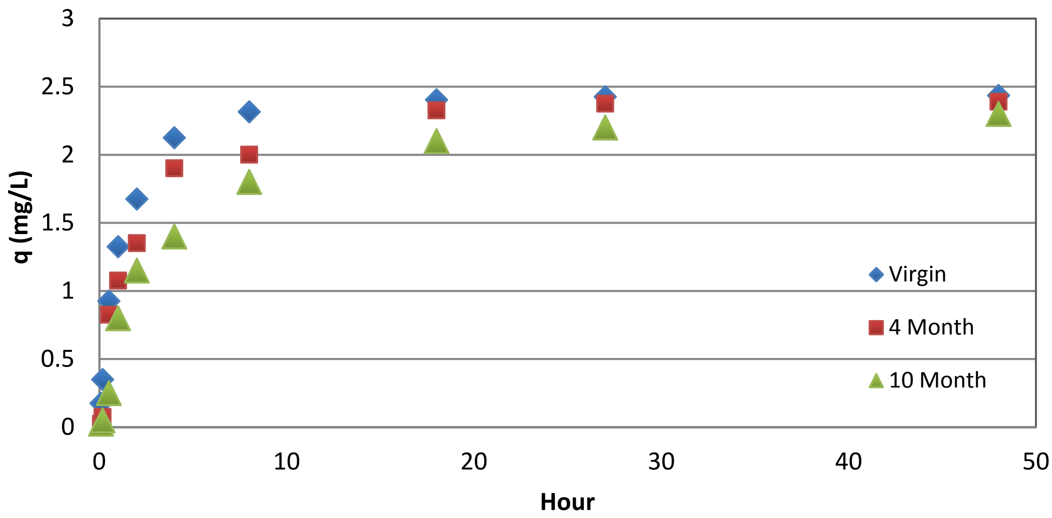


Figure 5.17 Kinetic curve for ammonia adsorption on zeolite at different service time

The assumption for pseudo-second-order model is the rate-limiting step may be a chemical sorption involving the exchange of electrons between adsorbent and adsorbate. The kinetic model is given as:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t$$

where q_e and q_t represented the adsorption capacity on the zeolite at equilibrium and time t, respectively. k_s is the pseudo-second-order rate constant (g/mg-min). The slope and intercept of plots of t/q_t versus t were used to determine the rate constant, k_s, and equilibrium capacity, q_e, by linear regression. The results are shown in Table 5-4. The experimental data were well fitted by the pseudo-second-order model (R^2>0.94). The rate constant k_s was reduced significantly after 4 months and 10 months of usage. This result indicated that the build up of biofilm may increase the zeolite service time by providing bioregeneration but can also decrease the zeolite adsorption rate. Therefore the maintenance of the adsorbent integrated system should involve certain type of biofilm removal to provide maximum value of adsorbents.

Table 5-4 Pseudo-second-order constants for zeolite at different service time

	Virgin	4 Month	10 Month
k_s (g/mg-min)	0.00721	0.00166	0.0012
R^2	0.99	0.93	0.94

5.3.4.2 EAC equilibrium and kinetic curve

Figure 5.18 showed the equilibrium curve of EAC after 0, 4 and 10 months of service time. The Freundlich equation was once again used to describe the adsorption isotherm. Table X presents the Freundlich equation parameters of adsorption capacity (K) and the strength of adsorption (1/n) for the EACs.

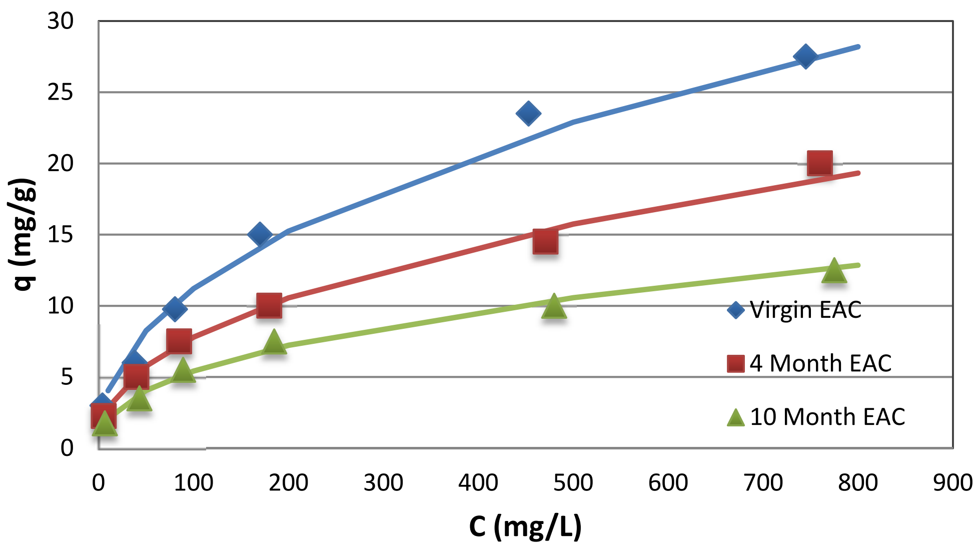


Figure 5.18 Equilibrium curve of EAC on COD adsorption

The results showed the EAC isotherms follow the Freundlich equation very well (R^2>0.98). The adsorption capacity parameter K was reduced from 1.46 to 1.05 and 0.8 after 4 month and 10 month usage, which corresponds to approximately 28% and 45% reduction, respectively. This result indicates that the microorganisms in the system were able to effectively regenerate EAC, but not as well as with zeolite.

Table 5-5 Freundlich constant for EAC at different service time

	Virgin	4 month	10 month
K	1.46	1.05	0.80
1/n	0.443	0.436	0.416
R^2	0.98	0.99	0.99

EAC COD adsorption kinetic curve data are shown in Figure 5.19, and the Lagergern pseudo-first-order equation was used to describe EAC kinetic curve (Tseng et al., 2015). The equation is given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_f t$$

where q_e and q_t are the amount of COD adsorbed at equilibrium and at time t. k_f is the pserudo-first-order rate constant (1/min). The slope and interception of plots of $\ln(q_e\text{-}q_t)$ versus time were used to determine k_f by linear regression.

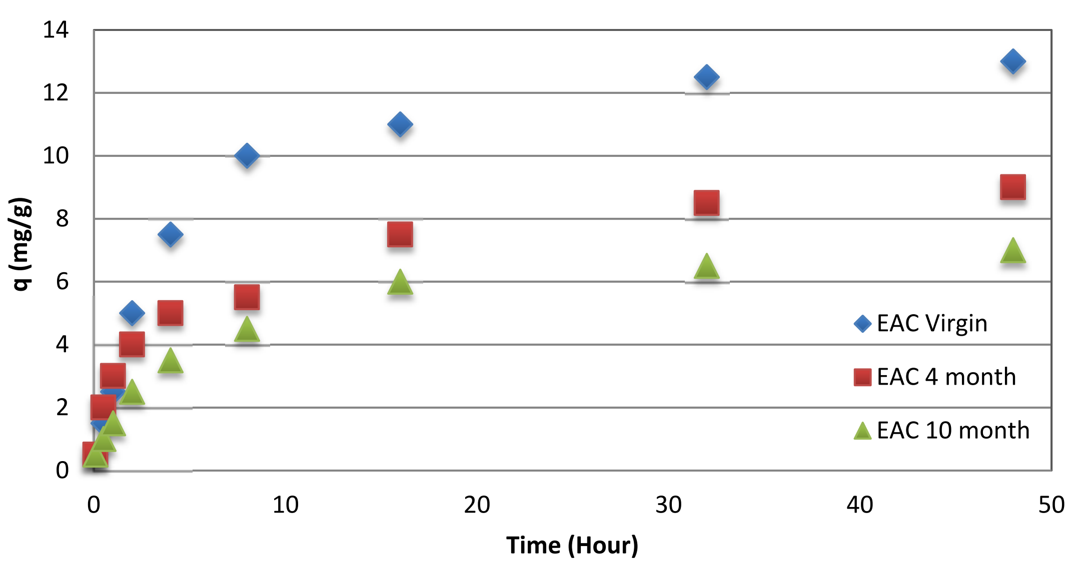


Figure 5.19 Kinetic curve on COD adsorption for EAC at different service time

As shown in Table 5-6, the rate constant k_f for virgin, 4 month and 10 month EAC were 0.00164, 0.0014 and 0.00137, respectively. These results showed the service time only slightly reduced the adsorption rate constant, which could indicate the biofilm built up over time wasn't the rate limiting step for EAC adsorption. Nassar et al. (2008) reported that the mass transfer for activated carbon can be described as external mass transfer and pore diffusion. The pore diffusion is the main rate limiting step for adsorption and is associated with 95% of adsorption capacity. Since bioregeneration wasn't able to regenerate activated carbon as well, thermal regeneration or replacement is required for the long term usage of activated carbon.

Table 5-6 Lagergern pseudo-first-order equation constant for EAC at different service time

	Virgin	4 Month	10 Month
k_f	0.00164	0.0014	0.00137
R^2	0.96	0.98	0.95

5.4 Conclusion

This study has successfully demonstrated the long-term benefits of integrating adsorbents into algal wastewater treatment systems. Mixing zeolite and activated carbon was shown to help the system maintain good wastewater treatment efficiency while treating PHWW continuously or in intermittent spikes. In the DOE Bioenergy Technology Office Multi Year Plan (2016), catalytic hydrothermal gasification (CHG) is proposed as PHWW treatment for nutrient recycling. However CHG is an energy intense process that involves significant investment and maintenance costs. Integrating adsorbents into algal wastewater treatment that treats PHWW is a better option with lower costs. Another benefit of integrating adsorbents is the increase of biomass productivity. This study has showed the integration of adsorbents can improve the biomass productivity, especially with PHWW addition. Although the biomass from the adsorbent integrated system had higher ash content, it still had higher overall energy yield per unit area. In future work, it would be advantageous to develop an ash reduction or mineral extraction process for biomass pretreatment prior to HTL conversion to improve efficiency and potentially produce some additional valuable products such as nanoparticulate SiO_2. This study also showed the adsorbents were still functional after 10 months of usage, but biofilm control may be needed for zeolite and replacement of adsorbents maybe required for activated carbon, which lost more than half of its original capacity after 10 months of usage, even with microbial bioregeneration.

6 TECHNO-ECONOMIC ANALYSIS OF A COUPLED ROTATING ALGAL WASTEWATER TREATMENT AND BIOCRUDE OIL PRODUCTION SYSTEM

6.1 Introduction

Looking towards the future, the world needs a cost-effective alternative for renewable fuels to help mitigate the economic and environmental concerns associated with our dependence on finite fossil fuel resources. One promising alternative replacing fossil fuels is biofuels derived from algal biomass that fixes carbon dioxide as it grows photosynthetically, and subsequently can be converted into biofuels and other useful biochemical products with significantly reduced carbon footprint. Certain algae species have shown the potential to supply enough bioenergy for the entire US transportation sector (35 quads per year) using only 20 million hectares (10% of arable US land) (Christi, 2007); however there are many technical and economic barriers that currently make it unfeasible to realize this tremendous potential. One of the earliest studies on algal biodiesel was conducted in Germany during the Second World War, due to the lack of hydrocarbon fossil fuels (Johansson et al., 2010). This study was primarily focused on microalgae cultivation in open ponds under nitrogen deficit conditions. Despite decades of intermittent research, and a large number of recent studies on algal biofuels, large-scale commercial production of algal biofuels has not yet been realized due to relatively high production costs in comparison to petroleum based fuels (Pfromm, 2010).

Over the last decade, the predominant approach to algal biofuels has focused on selectively growing high-oil algae and then extracting the algal oils for conversion to biodiesel via transesterification. When trying to scale-up this approach in outdoor settings, there are significant technical problems associated with (1) contamination of target high-oil algae by various low-oil organisms (non-target algae, bacteria, and grazers); and (2) high energy input for separation of algal oils from the aqueous media and other biomass components. These technical problems have significant cost impacts, and additionally, the major inputs for growing algae (water and nutrients) can also have a significant cost if they must be purchased. Altogether, these factors pose a significant challenge to the techno-economic viability of algal biofuels.

In order to address these problems, Zhou et al. (2013) proposed and analyzed the so-called environment-enhancing energy (E^2-Energy) process synergistically integrating algae cultivation with wastewater treatment. Combining algal biofuels and wastewater treatment can be facilitated by using hydrothermal liquefaction (HTL) to convert the whole wet biomass of algae and other co-cultivated organisms (mostly bacteria) into a bio-crude oil, which is a biofuel intermediate that is akin to crude petroleum. However, although the aqueous byproduct of HTL (PHWW) contains more than 80% of nutrients, it also contains toxic compounds that can inhibit the growth of algae (Biller et al., 2012). Several studies reported 50 to 100 times dilution is needed to prevent inhibition (Zhou et al., 2013; Pham et al., 2014). Jones et al. (2014) proposed a new process of combining whole algae HTL, hydrotreating the biocrude oil and using catalytic hydrothermal gasification (CHG) as PHWW cleanup method. Elliot et al. (2013) proved CHG can be an effective process for removing organics in PHWW by up to 99% and allows the nutrients to be recycled back to algae cultivation system. However, the cost of CHG is quite high, typically exceeding the cost of the HTL process because it uses higher temperatures and pressures as well as a catalyst.

The previous chapter showed that the adsorbents augmented Algaewheel® wastewater treatment system can maintain good performance under higher PHWW concentration. Therefore integrating adsorbents into an algae cultivation system allows PHWW be recycled without further pretreatment. This chapter develops a techno-economic analysis to compare three algal wastewater treatment and biofuel production scenarios: (1) Adsorbent amended Algaewheel®-HTL, (2) Algaewheel®-HTL-CHG and (3) High rate pond-Transesterification-Anaerobic digestion. To represent the commercial scale, all scenarios are estimated based on 100 hectares of algae cultivation area. For each scenario, the biomass production costs and final fuel production costs were estimated and then compared. Wastewater treatment credits were also taken into account for calculating minimum fuel selling price in each scenario. The results can be used to identify the bottlenecks of current technology and direct future algal biofuel technology development including the potential for integration with wastewater treatment.

6.2 Methods

6.2.1 System boundary

The system boundary started with the primary clarifier, algae cultivation, secondary clarifier, dewatering, drying (if needed), conversion of intermediate fuel, upgradation of finished fuel and nutrient recycle units. The major inputs of the system is domestic wastewater and the outputs are treated water and finished fuel. The focus of this study is to build an engineering model for wastewater treatment and fuel production plants, therefore the transportation and distribution cost is not included in this study.

6.2.2 Scenario description

Three scenarios were compared in this study: (1) Adsorbent amended Algaewheel®-HTL, (2) Algaewheel®-HTL-CHG and (3) High rate pond-Transesterification-Anaerobic digestion. The scenarios differ in three ways: (1) algae cultivation system (Algaewheel® system or high rate pond), (2) biofuel conversion methods (HTL or transesterification) and (3) nutrient recycling process (adsorbent integrated cultivation system for direct recycle, CHG or anaerobic digestion). A combined heat and power generator (CHP) was included in the scenarios with methane production. Scenario 3 is used as baseline condition since it is the predominant algal biofuel route in current industries (Lundquist et al., 2010).

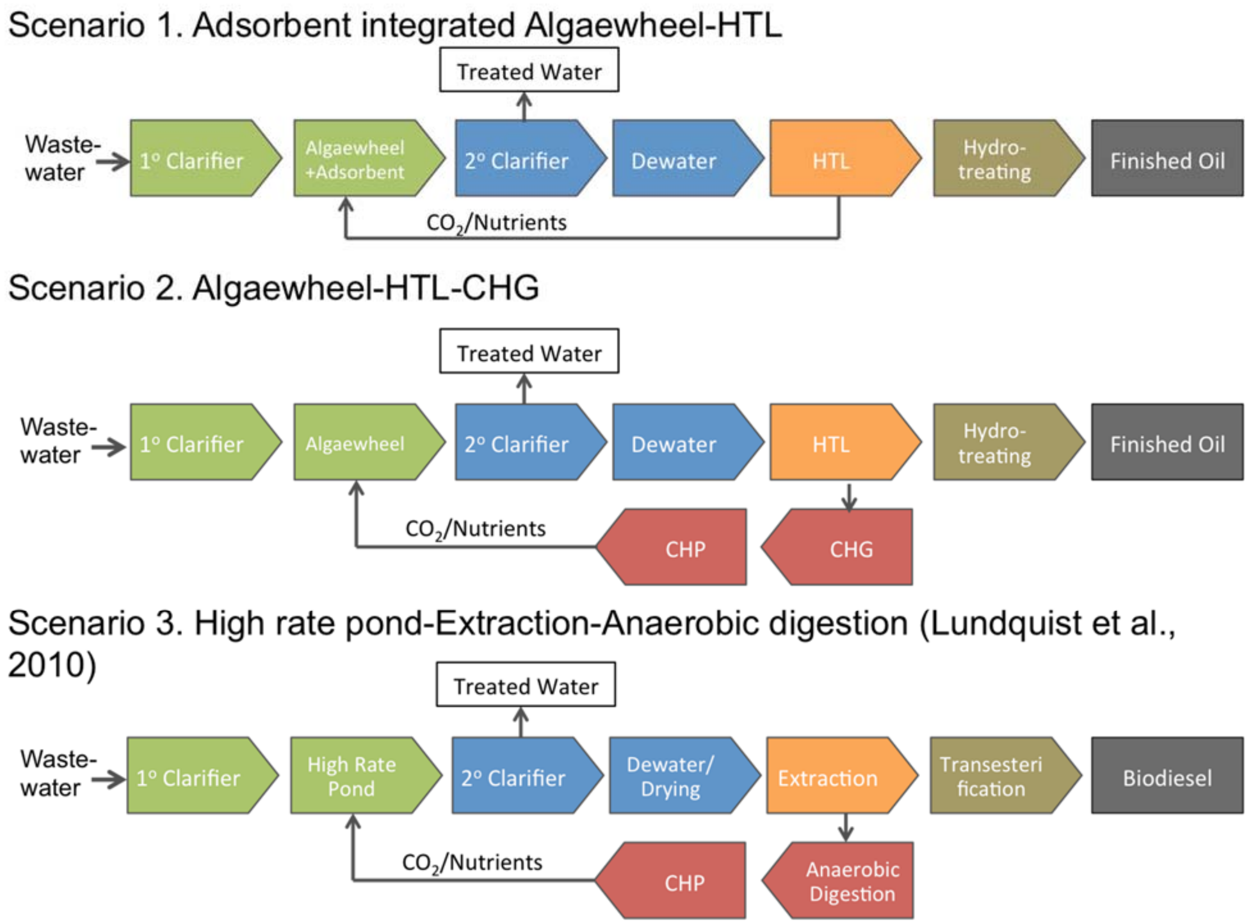


Figure 6.1 Summary of the three algal wastewater treatment and biofuel production scenarios

Low strength municipal wastewater was assumed to be the input water source for all cases. The concentration of the major parameters are: COD 500 mg/L, BOD: 200 mg/L and TN 35 mg/L (Hanze and Comeau, 2012). An Algaewheel® system was used in Scenario 1 and 2, while Scenario 3 used a conventional high rate pond. All of the algae cultivation facilities were assumed to be 100 hectares to represent commercial scale facilities. HRT of the cultivation systems were picked as the treated water had been proved to meet discharge regulation (BOD < 20 mg/L). Commercial Algaewheel® systems are generally operated with less than 1 day HRT for municipal wastewater application, set as 1 day HRT in this study; while high rate pond usually required 3 to 5 days (Lundquist et al., 2010), assumed to be 4 day HRT in this study. The coarse bubble aeration used to rotate the Algaewheel® system enhances heterotrophic growth and allows the Algaewheel® system to operate at a lower HRT. Additionally, because the depth of an Algaewheel® system is usually deeper than high rate pond, the amount of wastewater treated per unit area can be 8 times higher. Algaewheel® is a biofilm based cultivation technology, where the biofilm on the wheel naturally sloughs off the wheel due to rotating shear force and the sloughed biomass can be easily harvested in a clarifier. High rate pond systems rely on chemical or bioflocculation occurring in order to harvest biomass in clarifier. For all three scenarios, biomass was assumed to be solar dried to avoid large energy inputs for drying. Lundquist et al. (2010) reported solar drying for lipid extraction can be done within a day. For scenario 1 and 2, the biomass was dried to 20% solid content and then sent to continuous HTL facility for biocrude oil production. The crude oil products were then sent to the oil upgrading process to produce commercial drop-in fuel products. The post HTL wastewater (PHWW) was directly recycled back to adsorbents amended Algaewheel® system for scenario 1. In scenario 2, PHWW was processed by CHG to convert organics into methane and hydrogen. The nutrient-rich aqueous products then can be recycled back to the Algaewheel® system. The resulting biogas was burned for energy and heat by a combined heat and power generator (CHP) for facility utility. For scenario 3, the biomass is dried to at least 80% of solid content for lipid extraction. Extracted lipid were then converted into biodiesel through transesterification. The extraction residue were used to produce biogas by anaerobic digestion. The effluent of anaerobic digestion will be recycled back to the high rate pond for nutrient recovery. The biogas will be combined in CHP for on-site heat and energy usage.

6.2.3 Accuracy of the estimate

According to the cost estimation guidelines provided by the Association for Advancement of Cost Engineering (AACE), this study is considered as Class 4 Estimate which is the feasibility or pre-design Estimate. This class is prepared using cost curves and scaling factors for major processes. Cost accuracy ranges from -30% to +50%. The capital costs are estimated from a variety of resources. The original cost reflects the year of the cost estimate and the scale of the equipment. All capital costs were adjusted based on the inflation index between estimation year and 2016. The scale is adjusted to the match scale from original scale by using the following equation:

$$Scaled\ equipment\ cost\ =\ cost\ at\ original\ scale\ \times (\frac{scale\ up\ capacity}{original\ capacity})^n$$

where n is the scale factor, typically 0.6 to 0.7 (Jones et al., 2014).

6.2.4 Clarifiers and sludge dewatering

The primary clarifier is used to separate settleable biosolids from the raw wastewater, which is assumed to have a typical BOD concentration of 200 mg/L and a total nitrogen content of 35 mg/L as N (Metcalf and Eddy, 2003). 40% of the BOD was assumed to be captured in the sludge of the primary clarifier. The main design criteria for a clarifier is the retention time which is usually between 1 – 2.5 hrs and the weir overflow rate which ranges from 30 – 50 $m^3/m^2 \cdot d$ (Metcalf and Eddy, 2003). For a 500 MLD plant (scenario 1 and 2), 5,000 m^2 area is needed for the primary clarifier (1 hour HRT) and 10,000 m2 of area is needed for the secondary clarifier (2 hour HRT) when the depth of the clarifier is assumed to be 4.3 m. A total of 1.5 hectares of clarifier space is included in land requirement estimation. The size of primary and secondary clarifiers for scenario 3 will be 650 m^2 and 1300 m^2, respectively. The cost of the clarifier can be calculated based on the following equation (D. Digreforio, 1969):

$$log(Cost) = \frac{1}{0.233\log(Area) + 0.758}$$

where the cost unit is in dollars/ft^2 and Area is in thousands of ft^2. Inflation was taken into account to match the current cost.

Although HTL is able to process wet biomass, higher solids content is preferable due to higher energy return. Assuming the moisture content of settled solids from the clarifier is 99 to 99.5%, a max of 8,000 m^3/day wet biomass are then sent to a gravity thickener for scenario 1 and 2, which has an assumed capture efficiency of 95% with a nominally 3% solids concentration as output. With an HRT designed to be 4 hrs, the total volume required for gravity thickening is 1333 m^3. Solar drying was selected as the best method to dry the biomass with minimal additional energy input, and it was assumed to increase biomass solid content from 3% to above 20%. A shallow (1 cm) layer of algae slurry is spread over a low-density polyethylene liner to allow for drying within one day. Concrete tracks are laid down to allow a modified scrapper or vacuum truck to harvest the dried algae without damaging the liner.

6.2.5 Algae cultivation system

6.2.5.1 Algaewheel® system

The algae cultivation system used for scenario 1 and 2 was the Algaewheel® system, as provided by OneWater, Inc, which was used to develop and demonstrate improvements in algal biomass yield. Algaewheel® was selected because it is a proven, effective system for algal wastewater treatment that has been used for more than 10 pilot- and full-scale installations (Onewater Inc, 2016). Algaewheel® uses rotating wheel-shaped elements that enhance algal growth on the outer surface of the wheel, and have bacterial growth on the media and surfaces inside the wheel. The symbiotic growth of algae and bacteria increases overall biomass productivity as photosynthetic algae use CO_2 respired by heterotrophic bacteria, and bacteria use the O_2 produced by algae. This combination enhances algal growth by providing in-situ generation of CO_2 (a potentially costly input for algal growth) and by removing O_2 produced by photosynthetic algae, which can suppress algal growth if concentrations build up too high. As the wheel rotates by coarse bubble aeration (no motorized rotation), more surface area and algae are exposed to sunlight, thus improving biomass productivity while also providing better nutrient removal from the wastewater. Mixed-species algal biofilms continuously slough off the wheels by shear and can be readily collected by a screen or clarifier.

The capital cost of the Algaewheel® system is estimated based on the cost of wheels and the liner installation. As shown in Table 6-1, the cost of the Algaewheel® equipment is calculated based on the material cost and an installation fee. The Algaewheel® is made of HDPE because it has high durability and can float on water. A 10% installation fee was assumed in addition to the material cost. The areal cost of a Algaewheel® is 22.5 $\$/m^2$ based on information provided by the manufacturer. Lundquist (2010) suggested a clay-liner is better lining material over plastic liner because of the lower costs and better durability. Therefore, clay liners were assumed as the lining material ($\$3.4/m^2$) (Lundquist et al., 2010). The Algaewheel® system construction cost was assumed to be 20% of the Algaewheel® cost.

Table 6-1 Algaewheel® cost estimate parameters

Algaewheel Cost	
Material: HDPE ($/kg)	1.5
Unit wheel weight (kg)	5
Wheel material cost ($/wheel)	7.5
Assembling cost	0.75
Unit wheel price ($/wheel)	8.25
Number of wheel per m2	3
Unit area cost ($/m2)	22.5

6.2.5.2 *High rate pond*

High rate ponds have been used for commercial algae production since the 1980s. It is a shallow raceway pond usually equipped with paddlewheels for mixing. The depth of the high rate pond is between 0.2 to 0.4 m to avoid the dark zone that occurs at the bottom of the pond thus improving the light utilization efficiency. For this study, the depth is assumed to be 0.3 m. Mechanical mixing is necessary to enhance system biomass productivity. The channel flow velocity is usually between 0.15 to 0.5 cm/s to provide sufficient mixing without consuming too much energy. The major cost for high rate pond is dominated by the lining materials. Lundquist et al (2010) reported that even the cheapest plastic liner is twice the cost of a clay liner and the capital cost for 4 hectares of clay liner HRP is $136,000 (2010 value).

6.2.5.3 *Blower for Algaewheel®*

The course-bubble aeration used in the Algaewheel® system provides both oxygen and a motive force for rotating the wheels. Oxygen is necessary for heterotrophic microorganism to grow and remove organics in water. For the Algaewheel® system, oxygen was provided into the system in 3 ways: photosynthetic oxygen, surface diffusion and aeration. Each gram of BOD_5 removal requires 1.1 grams of O_2 (Oswald et al., 1953). Therefore, a system that reduces BOD from 120 mg/L to 24 mg/L at 500 MLD requires a total of 52.8 ton O_2/d. Oswald (1988) developed the following stoichiometric equation to describe algal photosynthesis as given:

$$106CO_2 + 236H_2O + 16NH_4^+ + HPO_4^{2-} \rightarrow C_{106}H_{181}O_{45}N_{16}P + 118O_2 + 171H_2O + 14H^+$$

Based on this equation, 1.55 grams of O_2 are produced per gram of algal biomass. In the adsorbents integrated Algaewheel®/HTL scenario, 28 tons of biomass was produced in the Algaewheel® system per day. Among 28 tons of biomass, 9.3 tons of biomass was produced photosynthetically according to equations in section 4.2.4. Therefore, 14.5 tons of oxygen was produced by algae every day. Surface diffusion can be estimated by a general mass balance equation (Jones and Stokes, 2003):

$$V \times \frac{dC}{dt} = K_L \times A \times (C_s - C)$$

where V= volume of water in contact with the surface (m^3)

A=area of water surface (m^2)

C=concentration of oxygen in water (mg/L)

Cs=saturated concentration of oxygen in water (mg/l) (8.3@25°C)

K_L=oxygen transfer velocity (m/day) $=\frac{2 \times water\ velocity(\frac{ft}{s})^{0.5}}{Depth(ft)^{0.5}}$

While assuming the dissolved oxygen concentration in water is 3 mg/L, water velocity 0.05 ft/s and 0.5m depth, the oxygen transfer rate is 6.7 g/m2/d. Therefore, a total of 31.6 ton of oxygen was needed from the aeration system. In order to estimate the airflow of the aeration, Bolles (2006) developed an equation to calculate standard oxygen transfer rate:

$$SOTR = \frac{OTR}{(\frac{\beta \times C_{S,T} - C_W}{C_{s,20}}) \times \alpha \times (\theta^{(T-20)})}$$

SOTR : standard oxygen transfer rate (lb O_2/hr)

OTR : oxygen transfer rate under process condition. (31.6 ton/day)

α : ratio of oxygen transfer efficiency in wastewater to OTE in tap water, 0.8 for course bubble diffuser

β : Cs(wastewater)/Cs(tap water), 0.95

θ : Arrhenius constant, 1.024

C_{ST} :Oxygen saturation concentration corrected for altitude and temperature, 8.19

C_W :Operating oxygen concentration, 3 mg/L

$C_{s,20}$: oxygen saturation concentration at tap water at 20°C, 9.02 mg/L

After calculation, SOTR is 6715 lb O_2/hr. Then convert SOTR into standard cubic feed per minute of air requirement (SCFM)

$$SCFM = \frac{SOTR}{60 \times \rho_{air} \times SOTE \times 0.23}$$

where

ρ_{air} : air density 0.0769 lb/ft^3

SOTE : standard oxygen transfer efficiency in clean water (0.05 @ 0.5m depth)

Therefore the minimum air flow rate for 100 hectare Algaewheel® system is 126,600 scfm or 0.13 scfm/m^2. Sedlak R. (1991) reported the install cost of diffused aeration system can be estimated as \$17/ lb O_2/hp-hr for blower and \$9.5/ lb O_2/d for diffuser system.

6.2.5.4 Biomass productivity

Algaewheel® wastewater treatment systems are practical, cost-effective, and readily scalable. Our research team partners at OneWater have been refining and up-scaling this algal wastewater treatment system for over a decade and have implemented facilities with wastewater treatment capacities of up to 120,000 gallons per day. Our previous results (Chapter 5) showed the total biomass productivity ranged from 16.8 to 28.2 (g/m^2/d) for the system without adsorbents and 28.3 to 33.6 (g/m^2/d) for the system with adsorbents. Based on the mass balance (Figure 6.2, Figure 6.3), the PHWW recycle concentration was below 0.2%. Therefore the biomass productivity used in Ad-AW/HTL scenario is 28 g/m^2/d and 26 g/m^2/d for AW/HTL/CHG scenario based on the results in the previous chapter. For the HRP/Ext/AD scenario, 22 g/m^2/d biomass productivity was assumed based on literature (Lundquist et al., 2010).

6.2.6 Biofuel intermediate production

The biomass feedstock is first converted into biofuel intermediate and can then be further upgraded into fuel. For Ad-AW/HTL and AW/HTL/CHG scenarios, the biomass was converted into biocrude oil via HTL, whereas the HRP/Ext/AD scenario converted algae to algae oil via solvent extraction.

6.2.6.1 Biocrude oil production

HTL converts feedstock into biocrude oil with elevated temperatures and pressures. The macromolecules in the feedstock are first depolymerized into smaller molecules and then the unstable fractions of chemicals are repolymerized into oil compounds (Demirbaş, 2001). According to our previous research (Dong et al., 2009; He et al., 2000; Yu et al., 2011a), HTL is more suitable for treating wet feedstock compared to other conventional thermochemical conversion approaches such as pyrolysis and gasification because: 1) the wet feedstock can be directly treated through HTL without any drying process; 2) the HTL conversion can produce bioenergy with a positive energy balance from low-fat and high-yield algae grown in wastewater (ASABE, 2009, 2011) as the results showed that up to 47 % of wastewater algae biomass can be converted into biocrude oil. Additionally, it was found that when the HTL reaction temperature reached 240°C, the biocrude oil products began to form as a self-separating asphalt-like products, which also address the dewatering issue of most algae biofuels approaches that rely on solvents to extract oils from dry biomass (Yu et al., 2011b).

The capital cost for HTL is based on the economic analysis conducted by Pacific Northwest National Lab (Snowden-Swen., 2016). The report was designed for a HTL system processing 100 dry tons of wastewater sludge per day, whereas this study proposed the HTL system to treat 41.5 ton of biomass per day for scenario 1. Using the exponential scaling method, the capital cost of HTL in this study is estimated to be

$$20{,}000{,}000 \times \frac{41.5\ ton/day}{100\ ton\ /day} = 8{,}300{,}000\ (\$)$$

The major energy input for HTL is the energy used for heating reactor. The energy input is:

$$E_{HTL}\ (\frac{Mj}{kg}) = \left[w_i C_{pw}(T - T_i) + (1 - w_i)C_{ps}(T - T_i)\right] \times [1 - r_h] \times \frac{1}{r_{eh}}$$

where w_i is the moisture content of the initial feedstock, C_{pw} is the specific heat of water (4.18 kJ/kg/K), C_{ps} is the specific heat of dry algae (1.25 kj/kg/K), T is the designated reaction temperature, T_i is the initial temperature, r_h is the heat recovery efficiency assumed to be 65%, and r_{eh} is the efficiency of electric heater assumed to be 90%.

6.2.6.2 Algae oil production

There are various methods for algal lipid extraction such as emulsification or cell breakage, however hexane extraction is the most economical method currently available. This process used for large scale soybean oil extraction, which is a reasonable model for estimating the design and cost of algae oil extraction. It is assumed the algae grown from high rate pond contains 25% lipid. Algal biomass was harvested from a secondary clarifier by auto-flocculation. The solids content was assumed to be 0.5 to 1%, which was then dewatered by a gravity belt thickener to increase the solids content to 3%. A solar drying bed was then used for further dewatering to achieve 20% solid contents. A gas fueled flash dryer was then used to bring the algae biomass solid content up to 95% and ready for solvent extraction. A centralized oil extraction facility is assumed to process 4000 ton of biomass per day as a typical commercial –

size soybean extraction facility. Therefore the extraction cost is estimated by the amount of the biomass extracted.

6.2.7 Biofuel upgradation

Biofuel upgrading is an essential process to polish the biofuel intermediate into commercial fuel. For HTL crude oil, hydrotreating process was selected to improve fuel quality. Similar to algae oil extraction, biocrude oil is assumed to be transported to a centralized hydrotreating facility. Biocrude oil is pumped in to a reactor and mixed with compressed hydrogen. The hydrotreating reactor is then heated up to 400 ^{o}C for 19 to 31 hours (Jones et al., 2014). During the hydrothreating, denitrification, desulfurization and oxygen reduction occurs while ammonia, hydrogen sulfide and CO_2 are producted (Snowden-Swan et al., 2016). In the BETO 2016 multi-year plan report, the estimated cost for biocrude oil hydrotreating is \$0.4/gal oil (BETO, 2016).

Transesterification is the fuel upgradation method selected for scenario 3, which converts algal lipid into biodiesel. A transesterification facility requires a continuously stirred reactor with a water or steam jacket to keep the reactor at 60^{o}C. Methanol is added into the reaction mixture to form esters. Methanol is more preferable than ethanol is because methanol is cheaper and easier to recovery at downstream process. Sodium methoxide is used as a catalyst because it requires lower concentration than sodium hydroxide and has already been employed in industrial biodiesel facilities (Haas et al., 2006). This study assumed the algae oil is transported to a centralized transesterification facility. Therefore the cost of transesterification will be the share of the facility cost and it will be \$0.3/gal oil (Haas et al., 2006).

6.2.8 Wastewater cleanup and nutrient recycle

6.2.8.1 Adsorbents integrated system

In our previous study, integrating adsorbents into a Algaewheel® system had been shown to improve both water treatment performance and biomass productivity. In addition, a mixture of activated carbon and zeolite adsorbents provided the best results. The results also showed that the adsorbent amended system was able to prevent microorganism communities from crashing due to higher PHWW concentration. Although the mass balance showed the PHWW recycle concentration is below 0.2%, there is still potential risk of toxic accumulation if not treated properly. Adsorbents can serve as a buffer to prevent toxic compound concentrations that would otherwise cause system failure. Our previous results also showed the service time of the adsorbents can be over 10 months even with a high PHWW concentration. In this analysis, adsorbent service time is conservatively assumed to be 1 year. The costs of the adsorbents are \$1000/ton for activated carbon and \$200/ton for zeolite (Alibaba, 2016). Each wheel was assumed to have 0.5 kg of activated carbon and 0.5 kg of zeolite added to it and would be reactivated every year. Cabot Inc (2016) provided off site service for adsorbents reactivation at 60% of original activated carbon price. 10% of additional cost was applied as an operation fee.

6.2.8.2 Catalytic hydrothermal gasification (CHG)

CHG was selected to be PHWW cleanup method for scenario 2. CHG has been proven to effectively remove 99% of COD in the PHWW and produce fuel gas like CH_4 and H_2 instead of just steam. CHG is considered to be a sister technology to HTL, both reaction involving high temperature and high pressure. The reaction temperature of CHG is between 325 to 350^oC. 7.8% Ru/C catalyst is used. The costs of CHG reactor were adopted from Jones et al. (2014).

6.2.8.3 Anaerobic digestion and combined heat and power generator (CHP)

Anaerobic digestion is used as a wastewater treatment and nutrients recycle method for scenario 3. The sludge of primary clarifier and extracted biomass were sent to an anaerobic digester. Anaerobic digestion is widely used in modern wastewater treatment plants. In an anaerobic digester, four processes take place to convert the organic matter in the waste into methane and carbon dioxide: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Typically about two third of volatile solid will break down in the anaerobic digester (Metcalf and Eddy, 2003). For these volatile organics, their chemical oxygen demand COD is 1.42 g O_2/g VS. A yield of 0.39 L CH4/g COD destroyed is commonly used to determine the methane yield. With the starting wastewater influent of 62 MLD to the primary clarifiers about 1.9 ton/day of sludge can be collected and sent to the anaerobic digester. The conversion of VS to methane can thus produce about a total of 3,200 m^3/d. With an assumed CHP efficiency of 80% (40% electricity and 40% heat), this amounts to just under 10 MWh/d that can be produced from the primary sludge and extracted biomass. The main design parameter is maintaining a long enough hydraulic retention time, which is affected by temperature during winter time. A typical hydraulic retention time of 30 days was chosen for the complete mix digester.

6.3 Results and Discussion

6.3.1 Mass balance

The mass balances of three scenarios are shown as Figure 6.2, Figure 6.3, and Figure 6.4. Detailed assumptions and parameters are listed in Appendix A. Scenario 1 (Ads-AW/HTL) had the highest intermediate fuel productivity of 4800 gal/day, where scenario 2 and 3 was 4550 and 1720 gal/day. The scenarios with Algaewheel® and HTL had much higher fuel productivity. It is due to (1) HTL had higher conversion ratio than oil extraction. HTL is able to convert 30 to 50% of biomass into crude oil (assumed 35% in this study), while the oil content of the wastewater grown algae is usually lower than 30% (assumed 25%). (2) HTL can also convert sludge collected from clarifier into crude oil. Additionally the Algaewheel® system had higher water process capacity, with the coarse bubble aeration, and was able to treat wastewater at less than 1 day HRT heterotrophically, which also increased the amount of collected sludge from the primary clarifier compared to scenario 3. Therefore, an additional 15.6 ton/day of sludge were converted into crude oil which accounted for 1400 gal/d of production. It is noteworthy that the sludge collected from clarifiers in scenario 3 was sent to an anaerobic digester for heat and electricity, which was used on-site to reduce imported energy cost.

The mass balances also showed the water quality of the effluent water for three scenarios. The results indicated that all scenarios had limited or no nitrogen removal. In fact, scenario 3 had a higher TN concentration in effluent than influent due to the nutrient recycle. Although the nitrogen profile study in chapter 4 showed most of nitrogen in effluent were nitrate rather than ammonia, it could still cause environmental problems such as eutrophication if not properly treated. Alternative application of portions of biomass could be one way to mitigate nitrogen level in the effluent. For example, similar to conventional municipal solid waste, collected biomass can be composted and then be used as fertilizer. Other options would be integrating nitrogen removal methods such as air stripping or struvite precipitation into the overall process scheme to make sure the effluent water quality will meet the discharge standards.

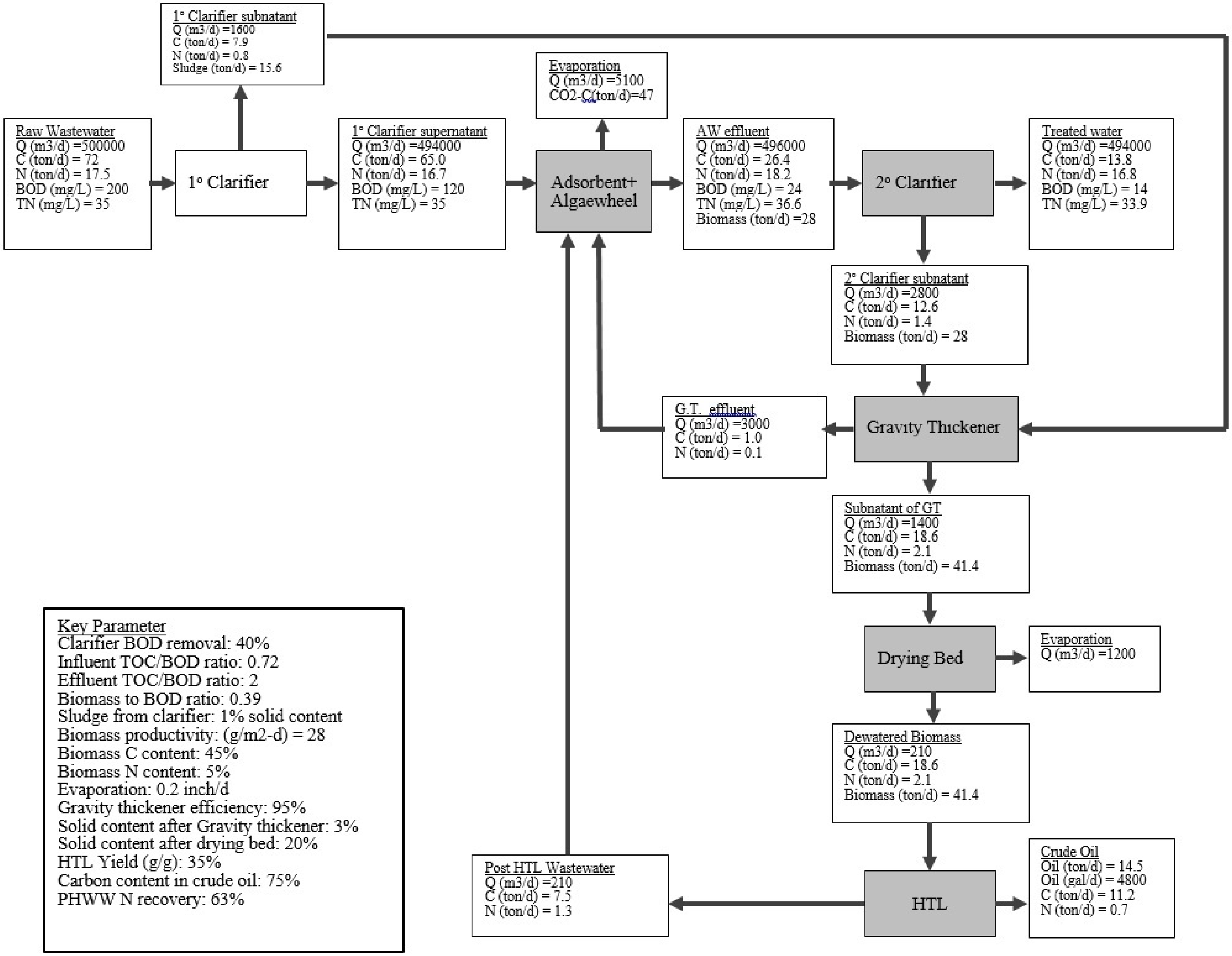


Figure 6.2 Mass balance of 500MLD Adsorbents integrated Algaewheel® system combined HTL

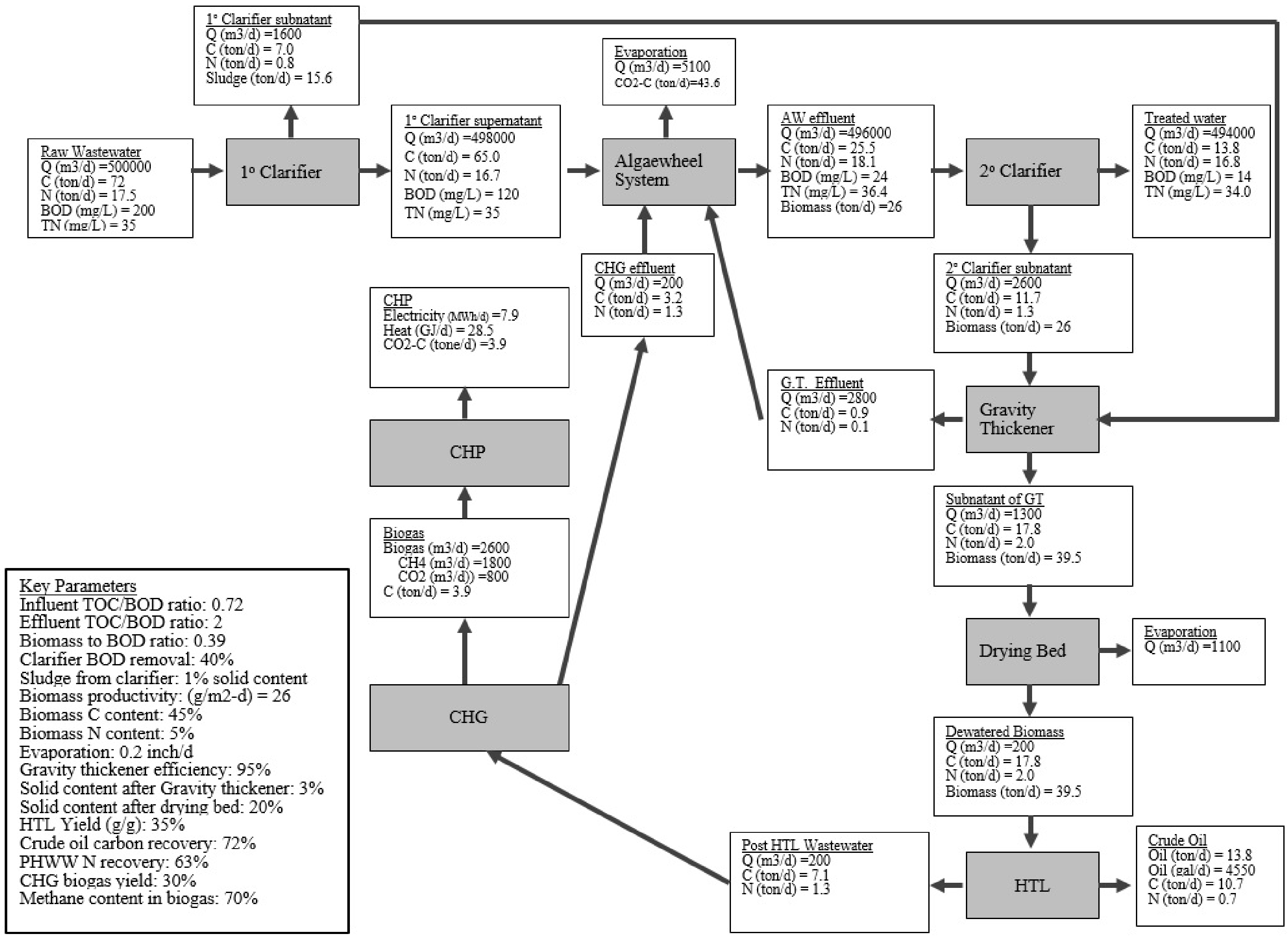


Figure 6.3 Mass balance of 500MLD Algaewheel® system combined HTL and CHG

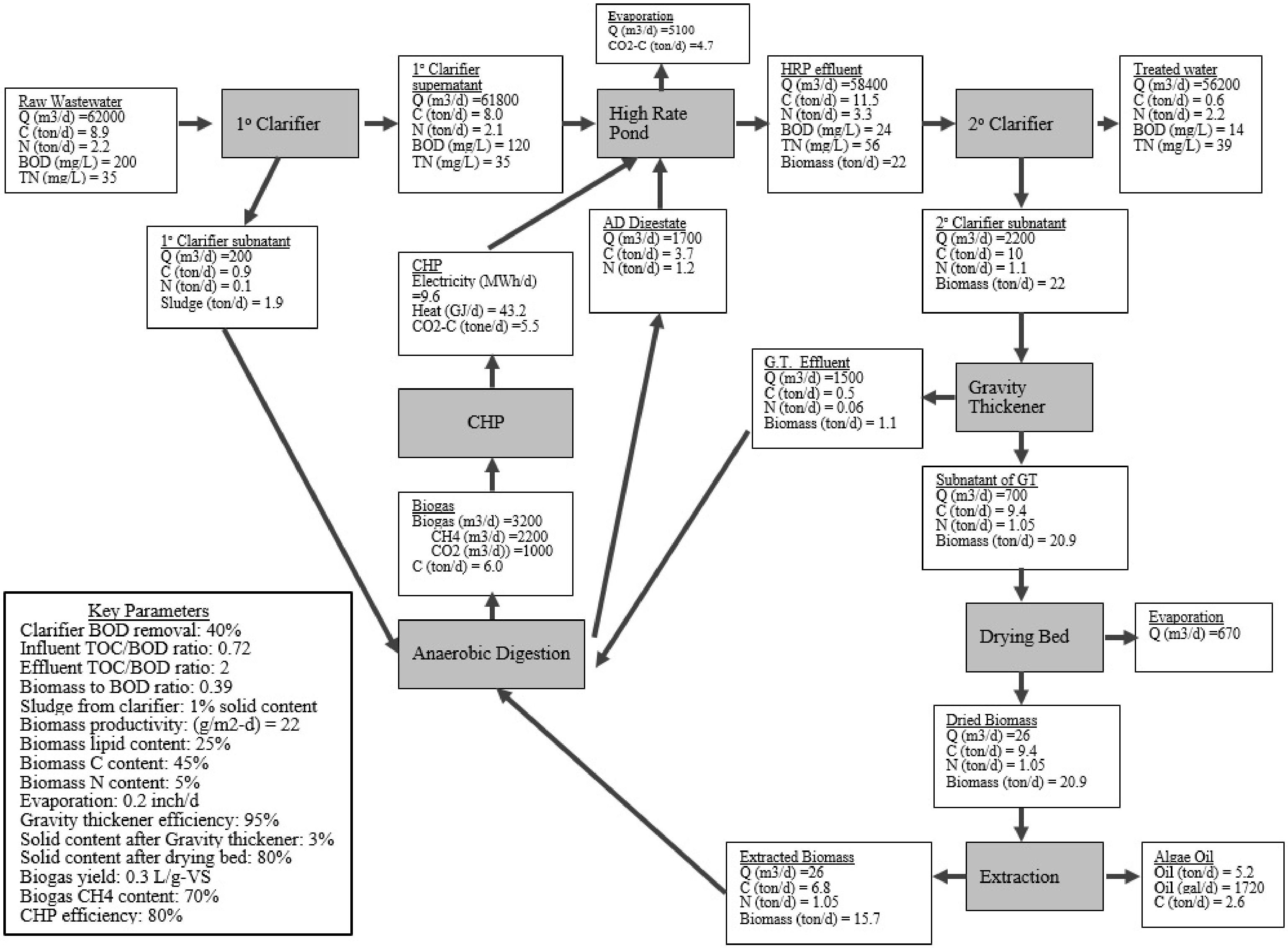


Figure 6.4 Mass balance of 62 MLD high rate pond system combined with extraction and anaerobic digestion

6.3.2 Biomass production cost

The biomass production costs for all three scenarios are shown in Table 6-2. All capital costs were scaled based on the biomass processed and adjusted for inflation. Detailed equipment costs are listed in Appendix B. For Algaewheel® system scenarios, the cultivation system plus aeration system consisted of 59% of the capital cost. On the other hand, the major cost for scenario 3 is land cost. This is because Algaewheel® system had much more complex infrastructure and designed for wastewater treatment. For O&M cost, electricity purchase is the major cost for scenario 1 and 2. Aeration for the Algaewheel® system accounted for more than 70% of the electricity cost. Overall, the biomass production cost for ad-AW/HTL, AW/HTL/CHG and HRP/Ext/AD scenario were $786, $821 and $659/ton. Although the biomass productivity of scenario 1 and 2 were double of high rate pond system, the biomass production cost is slightly higher. Davis et al. (2016) reported the algal biomass production costs with nutrient recycle at different scales. Their results showed the algal biomass costs between $392 to $649/ton. Our study had higher production cost because the assumptions of our study included the infrastructures for wastewater treatment.

Table 6-2 Biomass production cost for three scenarios

Capital	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Land	5,473,000	5,473,000	5,473,000
1. Clarifier	1,131,000	1,131,000	639,000
Algae Cultivation System	30,000,000	30,000,000	5,185,000
Aeration system	6,250,000	6,250,000	-
CO2 delivery	-	-	903,000
2. Clarifier	2,262,000	2,262,000	1,441,000
Thickeners	606,000	587,000	389,000
Drying beds	5,300,000	5,268,000	3,679,000
Water piping	5,240,000	5,240,000	2,524,000
Electrical	2,889,000	2,889,000	2,889,000
Buildings	91,000	91,000	91,000
Silo storage	83,000	83,000	83,000
Vehicles	76,000	76,000	76,000
Road and Fencing	257,000	257,000	257,000
Permit/construction management/Legal/Insurance	25,056,000	25,035,000	9,924,000
Capital depreciation (8%)	6,777,000	6,771,000	2,684,000

O&M	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Algae facility staff	748,000	748,000	748,000
Maintenance	1,193,000	1,192,000	473,000
Electricity purchase	1,700,000	1,680,000	322,000
Administrative staff	188,000	188,000	188,000
Insurance	90,000	90,000	90,000
Outside lab testing	25,000	25,000	25,000
Vehicle maintenance	8,000	8,000	8,000
Lab & office supplies	6,000	6,000	6,000
Employee training	5,000	5,000	5,000
Total O&M	3,962,000	3,941,000	1,864,000
Biomass productivity (ton/year)	14,000	13,000	7,000
Biomass production cost ($/ton)	**786**	**821**	**659**

6.3.3 Biofuel conversion cost

Table 6-3 shows the conversion cost for all three scenarios. HTL had much higher capital cost than the extraction facility because HTL involves high temperature and high pressure. HTL also consumed about twice the amount of energy than the lipid extraction plant. However, due to HTL having higher fuel conversion ratio than extraction (35% to 25%) in addition to higher biomass productivity, the breakdown conversion cost per fuel intermediate production is lower ($1.6/gal) compared to extraction ($3.4/gal).

Table 6-3 Conversion cost for three scenarios

Capital	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Flash Dryer	-	-	1,551,000
Extraction plant Share	-	-	3,695,000
HTL	8,745,000	8,344,000	-
Buildings	91,000	91,000	91,000
Silo storage	83,000	83,000	83,000
Vehicles	76,000	76,000	76,000
Road and Fencing	257,000	257,000	257,000
Permit/construction management/Legal/Insurance	3,886,000	3,717,000	2,416,000
Capital depreciation (8%)	1,182,420	1,131,120	735,210

O&M	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Maintenance	185,000	177,000	115,000
Extraction plant	-	-	478,000
Energy purchase	366,000	350,000	36,000
Administrative staff	188,000	188,000	188,000
Biomass hauling	239,000	239,000	239,000
Insurance	90,000	90,000	90,000
Outside lab testing	25,000	25,000	25,000
Vehicle maintenance	8,000	8,000	8,000
Lab & office supplies	6,000	6,000	6,000
Employee training	5,000	5,000	5,000
Total O&M	1,112,000	1,087,000	1,189,000
Fuel Yield (gal/yr)	1,399,000	1,335,000	564,000
Coversion cost ($/gal oil)	**1.6**	**1.7**	**3.4**

6.3.4 PHWW treatment and nutrient recycle cost

Table 6-4 shows the wastewater treatment cost for three scenarios. With an assumption of regeneration every year, adsorbents amended Algaewheel® system had the lowest nutrient recycle cost ($1.1/gal fuel production). The cost of CHG catalyst is also calculated based on the assumption of 1 year lifetime with the unit cost of $60/lb (Jones et al., 2014). It is surprised that

CHG and AD had similar nutrient recycle cost ($1.6/gal and $1.6/gal). The main reasons are the reactor size and biofuel productivity. In scenario 3, AD treated 1700 m^3 of wastewater per day while CHG only treated 200 m^3/day and the HRT of AD is 30 days comparing to CHG 's 1 hour HRT. The AD reactor size was more than three thousand times bigger than the CHG reactor. 67% of the inflow for AD was the supernatant of the gravity belt. Direct recycling of the supernatant to algae high rate pond is not possible because HRPs only rely on photosynthesis for oxygen production instead of aeration. Excess organic carbon source in the system could lead to anaerobic zone formation. Therefore if the system directly recycled the gravity belt thickener supernatant, it could end up causing the system to crash or become contaminated.

Table 6-4 Wastewater treatment and nutrient recycle cost for three scenarios

Capital	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Adsorbent	1,800,000		
CHG	-	3,596,000	-
Digestor	-	-	3,710,000
Biogas turbine	-	2,409,000	3,102,000
Permit/construction management/Legal/Insurance	756,000	2,522,000	2,861,000
Capital depreciation (8%)	204,000	682,000	774,000

O&M	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Adsorbents	1,260,000	-	-
Catalyst	-	1,055,000	-
Nature gas cost	-	338,000	-
Maintenance	36,000	120,000	136,000
Total O&M	1,296,000	1,513,000	136,000
Fuel Yield (gal/yr)	1,399,000	1,335,000	564,000
Nutrient recycle cost ($/gal oil)	**1.1**	**1.6**	**1.6**

6.3.5 Overall economic analysis

The minimum fuel selling price was determined as the selling price of the fuel that can make up the cost of production after including the value of by-products. Table 6-5 shows the summary of the fuel cost for all three scenarios and minimum fuel selling prices. Figure 6.5 shows comparison of the fuel production costs and areal fuel productivity with BETO estimation (BETO, 2016).

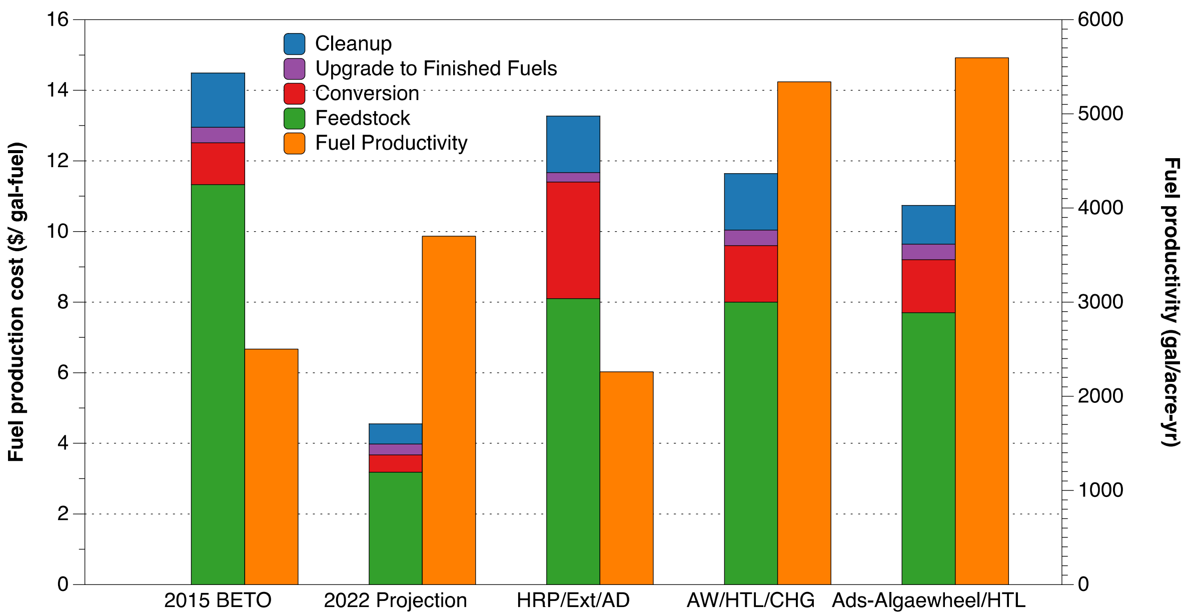


Figure 6.5 Comparison of fuel production costs and areal fuel productivity

In the BETO estimation, the fuel production cost was $14.78/gal. Comparing this cost to the production cost to scenario 1,2 and 3, which were $10.7, $11.7 and $13.2/gal. In BETO estimation, the feedstock cost alone $11.3/gal while Algaewheel® system feedstock costs less than $8/gal. And both AW/HTL scenarios production costs were lower than HRP/Ext/AD. The major difference was Algaewheel® system scenarios collected much more biomass (sludge) from wastewater. At 1 day HRT, about 40% of additional biomass can be harvested from from 1^{o} clarifier. Algaewheel® system was able to handle higher flow rate because of the fixed-film type cultivation method and aeration system. Fixed film system allows the large quantity of water to run through the system without washing out all the biomass. The aeration system provides oxygen for bacteria growth hence removing organics in water and providing good treatment.

Table 6-5 Production cost summary and minimum selling price for three scenarios

	Ad-AW/HTL	AW/HTL/CHG	HRP/Ext/AD
Feedstock ($/ton-biomass)	$785.7	$821.4	$659.5
Feedstock ($/gal-oil)	$7.7	$8.0	$8.1
Conversion	$1.5	$1.6	$3.3
Upgrade to Finished Fuels	$0.4	$0.4	$0.3
Wastewater Cleanup/Nutrient Recycle	$1.1	$1.6	$1.6
Balance of Plant			
Total Cost before Byproduct Credit ($/ gal)	**$10.7**	**$11.7**	**$13.2**
Byproduct Credit			
Energy Saving		$0.2	$0.9
WW Treatment Credit (BOD removal) ($/gal oil produced)	$29.8	$31.3	$9.2
Minimum Selling Price ($/gallon oil)	**-$19.11**	**-$19.78**	**$3.09**

The byproducts of the modeled process were energy saving and wastewater treatment credits. Energy saving was calculated based on the amount of biogas produced and utilized by CHP onsite to provide electricity and heat for the facility. The efficiency of the CHP was assumed to be 80% with 40% of electricity and 40% of heat produced from biogas. The electricity price was \$0.05/kWh and natural gas costs \$3.5/1000ft^3 (Nasdaq, 2016). The results showed the energy saving for AW/HTL/CHG scenario was $0.2/gal. It suggested Ad-AW/HTL scenario was still slightly preferable than Aw/HTL/CHG scenario in terms of overall fuel production cost even after energy saving credit. HRP/Ext/AD scenario still had the highest production cost after energy saving credits.

The wastewater treatment credits were calculated based on the amount of BOD removal. Typical municipal revenue of $1.23/kg BOD removed (AMSA, 2002). Both Algaewheel®

system scenarios received about $30/gal wastewater treatment credits and translate to negative minimum selling price. This indicated the revenue of wastewater treatment can cover all the fuel production cost thus all fuel were considered free. It is worthy to note that in this study, the cost accuracy ranged from -30% to +50%. However, even with +50% of production cost, wastewater treatment credit still exceeded fuel production cost. In addition, although the systems nitrogen removal was relatively small due to nutrient recycling, it could still have nutrient removal credits. EPA (2008) reported the nitrogen removal could cost between 1.91 to 2.39 $/lb with a traditional nitrogen removal system. Therefore it is worthwhile to develop different scenarios targeting nutrient removal.

6.3.6 Sensitivity analysis

The sensitivity analysis demonstrated the fuel production cost sensitivities to technical parameters. These parameters effect on the plant size, feedstock cost and fuel yields.

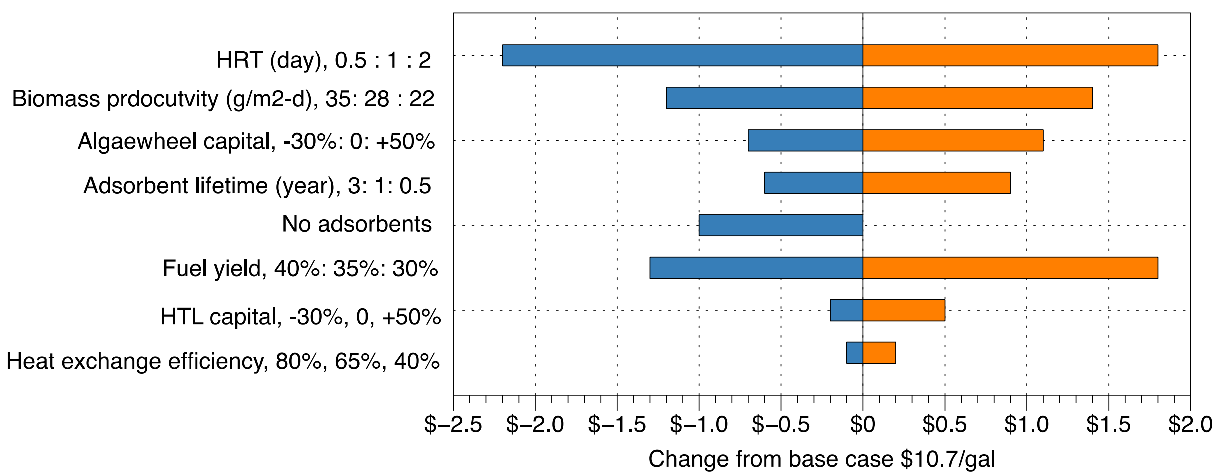


Figure 6.6 Sensitivity analysis of adsorbent integrated Algaewheel® with HTL system

Figure 6.6 shows the sensitivity test of different technical parameters at improve, baseline and poor conditions for Algaewheel®-HTL system. Among the eight parameters analyzed, the weight of Algaewheel® HRT is the most sensitive factor that impacts the fuel oil production cost. Since the harvested sludge consisted about 40% of the overall processed biomass at 1 day HRT, the change of HRT will also directly affects the amount of harvested biomass in the system. In addition, the amount of wastewater treated also affected the wastewater treatment credits. OneWater Inc had demonstrated Algaewheel® system at 6 hour HRT in various locations and performed well (personal communications, 2015). However it is unclear if the system is able to maintain good treatment with nutrient recycling at 6 hour HRT. Since HRT is the most sensitive factor and relative easy to improve, it is worthwhile to further investigate the limitation of lower HRT in field test.

The cost change associate with the capital of Algaewheel® and HTL were also analyzed. The result showed the uncertainty range of the estimation of this model (-30% to +50%). The capital cost of Algaewheel® had more significant impact on fuel production cost than HTL system. This analysis included the lifetime of adsorbents and potential of not using adsorbents. Our study showed even without adsorbents, PHWW can be recycled back to Algaewheel® system at 1% concentration without negative impacts on biomass productivity. However, Garcia Alba et al. (2013) found continuous PHWW recycle could cause the toxic compound build up and inhibit the growth of algae. On the other hand, our results showed adsorbents can prevent system from crashing with over 1% of PHWW recycle over 5 month. With 10 month of usage, the adsorbents still had over 50% capacity. Since the PHWW recycle concentration was less than 0.2% in the modeled condition, it is safe to assume the adsorbents service time can exceed 1 year. However, periodic wash to remove surface biofilm might be needed to improve adsorption rate on zeolite.

HTL biocrude oil yield also significantly impacts on the fuel production cost. Guo (2012) reported that the average biocrude oil yield from microalgae was 36.7% (AFDW). The biocrude oil yield for municipal sludge was 46.5% (AFDW). However, our operation results showed the biocrude oil yield from the Algaewheel® harvested biomass was only 30% (AFDW). The main factor responsible for the low crude oil yield is the high ash content in harvested biomass. There was close to 40% of ash present in the harvested biomass. Ash content is known to have negative effects on biocrude oil formation thus reducing biocrude oil yield (Chen et al., 2014). Therefore pretreatment technologies such as dilute acid soak can reduce the biomass ash content prior to HTL can be helpful in improving biocrude oil yield.

6.4 Conclusions

This study successfully constructed technical-economic analysis models to compare three different algal wastewater treatment coupled with biofuel production scenarios. Adsorbent integrated Algaewheel® system coupled with HTL had the lowest biofuel production cost ($10.7/gal). It is because of adsorbents stimulated higher biomass productivity and avoided CHG thus reduced nutrients recycle cost. The wastewater treatment credit analysis showed the negative minimum fuel selling price suggested that revenue from treating wastewater can cover the capitals used for fuel production. Extra revenue generated also indicated the proposed system is competitive with the traditional wastewater treatment systems. The future studies for reducing fuel production cost include: 1.) reducing HRT of the Algaewheel® system. Reducing HRT simultaneously increases harvested biomass and wastewater treatment credits, which is the most promising approach to further improve the economics. 2.) Improving HTL biocrude oil yield by optimizing HTL reaction condition and biomass pretreatment. 3.) Study the regeneration cycle and optimal adsorbents mixed ratio for improving biomass productivity. 4.) Evaluate the environmental sustainability metrics.

7 SUMMARY AND RECOMMENDATION

7.1 Summary

Microalgae are treated as suitable feedstock for next generation biofuel production because of the fast growth rate and high photosynthetic efficiency. Additionally, the ability to grow in marginal land and capable on uptake nutrient from wastewater reduces the impacts on other food crops. However, integrating algal cultivation with wastewater treatment posed several challenges such as high HRT thus requires large land area, difficulties of harvest suspended algae and potential of contamination. This study proposed a novel idea of integrating different types of adsorbents into algae cultivation system to facilitate integration with wastewater treatment and improve biofuel production. The main findings of this study are summarized as follow:

(1) Adding adsorbents into either suspended or fixed film growth algae cultivation can improve both biomass productivity and wastewater treatment performance. In the sequencing batch experiments, the ammonia removal percentage increased from 74.2% to 81.5% after addition of zeolite; the SCOD removal percentage increased from 77.5% to 89.1% after addition of GAC. The biomass productivity increased from 173 mg/L/day to 257.2 and 238.8 mg/L for the batch with zeolite and GAC. In the Algaewheel® system continuous operation test, adsorbents integrated systems were proved to be constantly had better COD and ammonia removal. The biomass productivity was increased by 8.9% for systems with adsorbents.

(2) Mixed Adsorbents had better performance than individual adsorbent. Mixed different adsorbents allowed the system had higher COD and ammonia removal than just activated carbon or zeolite. It is because different types of adsorbents can remove

different toxins and reserve different nutrients. By mixing adsorbents, algae grow in a more favorable environment hence improved biomass productivity.

(3) System is more stable with adsorbents. The experiment results showed more stable effluent quality regardless day or night for the system with adsorbents. Especially in spike loading condition, system with adsorbents had less fluctuation and recover faster than system without adsorbents. Therefore adsorbents integrated system provides steadier effluent quality, which can be useful for facilities constantly recycle water.

(4) Adsorbents can serve as PHWW treatment. This study compared the system performance with or without adsorbents while recycling different concentration of PHWW. The results showed the biomass productivity for system without adsorbent dropped significantly when PHWW concentration above 1.5% while the system with adsorbents had improved biomass productivity even at 2% PHWW concentration. This is strong evidence that PHWW consists some toxic compounds and adsorbents are able to mitigate the toxicity. In addition to prevent system from crashing, adsorbents also allows microorganism to utilize the nutrients in PHWW.

(5) Adsorbents' service time can exceed 10 month. The kinetic and capacity of adsorbents at different service time were tested. Although the capacity of EAC reduced 40% after 10 months usage, it was still able to maintain the system stability while 2% PHWW addition. On the other hand, the kinetic analysis showed zeolite's ammonia adsorption rate was reduced significantly. Therefore periodically removal of surface biofilm might be needed for zeolite.

(6) Adsorbents integrated Algaewheel® system coupled with HTL showed to most favorable TEA results. The system had the lowest biofuel production cost ($10.7/gal) comparing to other scenarios because of higher productivity and reduced nutrients

recycle cost by integrating adsorbents. Wastewater treatment credits are essential for making minimum fuel selling price competitive with current petroleum price. HRT and biocrude oil yield are the top two factors had the highest impact on fuel production cost. Researches reduce HRT and enhance crude oil yield can greatly improve the fuel production cost.

(7) Diatoms dominated the adsorbents integrated system. Nitzschia incospicua was found to dominate the adsorbent integrated Algaewheel® system. Zeolite can release silicon into water overtime and enhance the growth of diatom. Diatoms are favorable in wastewater treatment system because of the ability to utilize organic while light level is low. However, the ash content in diatom biomass could pose problems on formation of crude oil thus reduces crude oil yield.

7.2 Recommendations and Future Work

This study had showed the benefits of integrating adsorbents with algal wastewater treatment system and the first research to demonstrate a continuous PHWW feeding/treatment system in pilot scale. The results proved integration of adsorbents is a cheaper alternative for PHWW treatment. Based on TEA, HRT of the algal wastewater treatment played the most important role for biofuel productivity and economics of the minimum selling price. In order to facilitate the commercialization of algal wastewater treatment and biofuel production system, some recommends and future work are as follow:

(1) Investigate the effect of different adsorbents and mixing ratio for different algae and wastewater. This study selected activated carbon and zeolite for organic and ammonia removal. Other adsorbents such as bentonite and kaolinite can also be used for to the ability to adsorb phosphorus. Different mixing ratio of adsorbents can alter the micro environments in

water thus favor different species algae growth. Careful design of adsorbents types and mixing ratio to provide optimal wastewater treatment performance and biomass quality.

(2) Develop proper adsorbents integration methods for algal cultivation system and evaluate the adsorbent regeneration periods. Current adsorbents integration method was directly adding adsorbents granules inside Algaewheel®s. Although the wheel rotation provided mixing for adsorbents, significant biofilm built up on adsorbents were observed. In addition, it was difficult to replace adsorbents if needed since the wheels were sealed with screen meshes. Better integration method need to be developed. The kinetic and equilibrium analysis of 10 months service time adsorbents indicate the decay of adsorbents and required some maintenance such as remove biofilm or regeneration. The periods of regeneration need further experiments to determine.

(3) Study the effects of lower HRT and long-term effects of continuous PHWW recycle. This study showed lower HRT provides more biomass and wastewater treatment credits, which can be beneficial for commercialization. However, high wastewater flow rate also indicates more organics enters the system, which favors the heterotrophic microorganism growth and has the risk of reduce algae production. Proper balance of heterotrophic and autotrophic growth is essential to maximize biomass productivity and reduce operation cost. Although this study showed the Algaewheel® system is able to tolerate low PHWW concentration dosage without adsorbents, there is still potential for toxic compounds accumulation within the system after long-term operation. Long term operation of continuous PHWW recycling experiments need to be done to validate the accumulation effects.

(4) Develop biomass pretreatment process to improve product value and HTL yield. The biomass harvested from Algaewheel® system was found to have more than 30% of ash.

High ash content is known to reduce the HTL crude oil yield, decrease conversion energy efficiency and might reduce catalyst lifetime if used. Therefore it is important to develop pretreatment process that can decrease ash content before conversion. For example, dilute acid treatment is effective to remove calcium in biomass.

(5) Conduct Life-cycle assessment to evaluate environmental impacts. Considering the fact that most of biomass in Algaewheel® system were produced heterotrophically, the net CO_2 reduction is questionable comparing to other algal cultivation system. Therefore a detail LCA and energy balance analysis is needed to assess the carbon emission of the overall system with different scenarios.

References

Abeliovich, A. and Y. Azov. 1976. Toxicity of ammonia to algae in sewage oxidation ponds. *Applied and Environmental Microbiology* 31(6): 801-806.

Agrawal, S. and S. Gupta. 2009. Survival and Reproduction of Some Blue-Green and Green Algae As Affected by Sewage Water, Fertilizer Factory Effluent, Brassica Oil, Phenol, Toluene and Benzene. *Folia microbiologica* 54(1): 67-73.

Aktaş, Ö. and F. Çeçen. 2007. Bioregeneration of activated carbon: A review. *International Biodeterioration & Biodegradation,* 59(4): 257-272.

Amin, S. 2009. Review on biofuel oil and gas production processes from microalgae. *Energy Conversion and Management 50(7): 1834-1840.*

AMSA (2002). The 2002 Financial Survey: A National Survey of Municipal Wastewater Management Financing and Trends, Association of Metropolitan Sewerage Agencies.

Anastasakis, K. and A. B. Ross. 2011. Hydrothermal liquefaction of the brown macro-alga Laminaria saccharina: effect of reaction conditions on product distribution and composition. *Bioresource technology* 102(7): 4876-83.

Andersen, R. A. 2005. *Algal culturing techniques.* Academic Press.

Aparicio, M. A., M. Eiroa, C. Kennes and M. C. Veiga. 2007. Combined post-ozonation and biological treatment of recalcitrant wastewater from a resin-producing factory. *Journal of hazardous materials* 143(1-2): 285-290.

Appleford, J. M. 2005. Analyses of the products from the continuous hydrothermal conversion process to produce oil from swine manure. PhD diss. Urbana, IL: University of Illinois at Urbana-Champaign.

ASAE. 2005. Manure Production and Characteristics, ASAE D384.2. *American Society of Agricultural Engineers*.

Asano, T. 2007. *Water reuse: issues, technologies, and applications.* New York: McGraw-Hill.

ASTM. 2004a. ASTM D95-99: Standard test method for water in petroleum products and bituminous materials by distillation. In *Annual Book of ASTM Standards,* ed. ASTM, West Conshohocken, Pa.: Am. Soc. for Testing Materials.

ASTM. 2004b. ASTM D473-02: Standard test method for sediment in crude oils and fuel oils by the extraction. In *Annual Book of ASTM Standard,* ed. ASTM, West Conshohocken, Pa.: Am. Soc. for Testing Materials.

ASTM. 2004c. ASTM D4072-98: Standard test method for toluene-insoluble (TI) content of tar and pitch. In *Annual Book of ASTM Standards,* ed. ASTM, West Conshohocken, Pa.: Am. Soc. for Testing Materials.

Becker, E. 1994. Large-scale cultivation. *Microalgae: Biotechnology and Microbiology.Becker EW, Ed., Cambridge University Press: New York*163-171.

Berger, L. R. 1971. Effects of Hydrostatic Pressure on Photosynthesis and Growth of Unicellular Marine Algae and Diatoms. Second annual progress report.

Beevi, U.S., Sukumaran, R.K., 2014. Cultivation of microalgae in dairy effluent for oil production and removal of organic pollution load. Bioresour. Technol. 165, 295– 301

Biller, P. and A. B. Ross. 2011. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource technology* 102(1): 215-225.

Biller, P., A. B. Ross, S. C. Skill, A. Lea-Langton, B. Balasundaram, C. Hall, R. Riley and C. A. Llewellyn. 2012. Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. *Algal Research* 1(1): 70-76.

Bordovsky, J. P. and W. M. Lyle. 1998. Cotton irrigation with LEPA and susurface drip systems on the southern high plains. In Proc. Beltwide Cotton Conf., San Diego, CA., Jan. 5-9, 1998. pp. 409-412.

Boundy, B., S. Diegel W., L. Wright and S. Davis C. 2011. Biomass Energy Data Book: Edition 4.

Brown, T., P. Duan and P. Savage. 2010. Hydrothermal Liquefaction and Gasification of Nannochloropsis sp. *Energy fuels* 24(6): 3639-3646.

Brune, D. E., Schwartz, G., Eversole, A. G., Collier, J. A., & Schwedler, T. E. (2003). Intensification of pond aquaculture and high rate photosynthetic systems. *Aquacultural Engineering*, *28*(1-2), 65–86. doi:10.1016/S0144-8609(03)00025-6

Carmona, M. 2009. Anaerobic catabolism of aromatic compounds: A genetic and genomic view. *Microbiology and molecular biology reviews* 73(1): 71-133.

Carrère, H., C. Dumas, A. Battimelli, D. J. Batstone, J. P. Delgenès, J. P. Steyer and I. Ferrer. 2010. Pretreatment methods to improve sludge anaerobic degradability: A review. *Journal of hazardous materials* 183(1–3): 1-15.

Carvalho, A. P. and F. X. Malcata. 2001. Transfer of carbon dioxide within cultures of microalgae: Plain bubbling versus hollow-fiber modules. *Biotechnology progress* 17(2): 265-272.

Carvalho, A. P., L. A. Meireles and F. X. Malcata. 2006. Microalgal reactors: A review of enclosed system designs and performances. *Biotechnology progress* 22(6): 1490-1506.

Cabot Reactivation Services. Retrieved December 13, 2016, from http://www.cabotcorp.com/solutions/products-plus/activated-carbon/reactivation-services

Cary Jackson. 2014. TOTAL ORGANIC CARBON AND ITS FUTURE AS A REGULATORY TOOL FOR MONITORING AND REPORTING (Power point Slide) Retrieved from : http://www.weat.org/Presentations/2014lab_Jackson.pdf

Chen, H., G. Yang, Y. Feng, C. Shi, S. Xu, W. Cao and X. Zhang. 2012. Biodegradability enhancement of coking wastewater by catalytic wet air oxidation using aminated activated carbon as catalyst. *Chemical Engineering Journal* 198-19945-51.

Chen, Y. 2008. Inhibition of anaerobic digestion process: A review. *Bioresource technology* 99(10): 4044-4064.

Chisti, Y. 2007. Biodiesel from microalgae. *Biotechnology Advances* 25(3): 294-306.

Christenson, L.B., R.C. Sims Rotating algal biofilm reactor and spool harvester for wastewater treatment with biofuels by-products. Biotechnol. Bioeng., 109 (2012), pp. 1674–1684

Clarens, A. F., E. P. Resurreccion, M. A. White and L. M. Colosi. 2010. Environmental Life Cycle Comparison of Algae to Other Bioenergy Feedstocks. *Environmental Science Technology* 44(5): 1813-1819.

Clesceri, L. S., A. E. Greenberg and D. E. Andrew. 1999. *Standard methods for the examination of water and wastewater.* New York: American Public Health Association.

Craggs R, Sutherland D, Campbell H (2012) Hectare-scale demonstration of high rate algal ponds for enhanced wastewater treatment and biofuel production. J Appl Phycol 24:329–337

D. DiGregorioCost of Wastewater Treatment Processes Contract No: 14-12-60 (Thirteenth Edition), Federal Water Pollution Control Administration, Cinicinnati, Ohio (1968)

Daly, P. G. and C. C. Shen. 1988. The Deep Shaft Biological Treatment Process. In 479. 43rd Proceedings of Industrial Waste Conference.

Dan Knorr, John Lukas, and Paul Schoen: Harris Group Inc., & Biddy, N. T. M. M. J. (2013). Production of AdvancedBiofuels via Liquefaction, 1–90.

Das, P., Aziz, S. S., & Obbard, J. P. (2011). Two phase microalgae growth in the open system for enhanced lipid productivity. *Renewable Energy*, *36*(9), 2524–2528. doi:10.1016/j.renene.2011.02.002

De Jonge, R. J., A. M. Breure and J. G. Van Andel. 1996. Bioregeneration of powdered activated carbon (PAC) loaded with aromatic compound. *Water research* 30(4): 875-882.

Debabrata Mazumder and D. Mazumder. 2010. Removal of high organics containing wastewater in a shaft-type activated sludge hybrid reactor. *International Journal of Environmental Sciences* 1(3): 368-382.

Delrue, F., Y. Li-Beisson, P. -. Setier, C. Sahut, A. Roubaud, A. -. Froment and G. Peltier. 2013. Comparison of various microalgae liquid biofuel production pathways based on energetic, economic and environmental criteria. *Bioresource technology* 136(0): 205-212.

DOE. 2011. US Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry.

Dote, Y., S. Inoue, T. Ogi and S. Yokoyama. 1996. Studies on the direct liquefaction of protein-contained biomass: The distribution of nitrogen in the products. *Biomass and Bioenergy* 11(6): 491-498.

Dote, Y., S. Yokoyama, T. Minowa, T. Masuta, K. Sato, S. Itoh and A. Suzuki. 1993. Thermochemical liquidization of dewatered sewage sludge. *Biomass and Bioenergy* 4(4): 243-248.

Du, Z., B. Hu, A. Shi, X. Ma, Y. Cheng, P. Chen, Y. Liu, X. Lin and R. Ruan. 2012. Cultivation of a microalga Chlorella vulgaris using recycled aqueous phase nutrients from hydrothermal carbonization process. *Bioresource technology*(0): .

Eaton, A. D., & Franson, M. A. H. (2005). Standard Methods for the Examination of Water & Wastewater.

Eng, K. S., Bechtel, R., & Hutchenson, D. (2003). Adding a potassium, clinoptilolite zeolite to feedlot rations to reduce manure nitrogen losses and its impact on rumen pH, E. coli and performance. *Proc South West Nutrition*

Elliott, D. C. 1992. Evaluation of wastewater treatment requirements for thermochemical biomass liquefaction. PNL-SA-20267; CONF-920522--1.

Elliott, D. 2007. Historical developments in hydroprocessing bio-oils. *Energy fuels* 21(3): 1792-1815.

Ersahin, M. E., H. Ozgun, R. K. Dereli and I. Ozturk. 2011. Anaerobic treatment of industrial effluents: An overview of applications. *Waste Water—Treatment and Reutilization*.

Fachini, A., & Vasconcelos, M. T. (2005). Enhancing Diatom Growth by Using Zeolites to Change Seawater Composition (4 pp). *Environmental Science and Pollution Research - International*, *13*(4), 238–241. doi:10.1065/espr2005.12.287

Folch, J., M. Lees and G. Stanley. 1957. A simple method for the isolation and purification of total lipides from animal tissues. *Journal of Biological Chemistry* 226(1): 497-509.

Grange, P., E. Laurent, R. Maggi, A. Centeno and B. Delmon. 1996. Hydrotreatment of pyrolysis oils from biomass: reactivity of the various categories of oxygenated compounds and preliminary techno-economical study. *Catalysis Today* 29(1–4): 297-301.

Garcia Alba, Laura, M. Vos, C. Torri, D. Fabbri, S. Kersten, D. Brilman. 2013. “Recycling nutrients in algae biorefinery.” ChemSusChem Communications, 6:1330-1333.

Godos, I. de, Blanco, S., García-Encina, P. A., Becares, E., & Muñoz, R. (2009). Long-term operation of high rate algal ponds for the bioremediation of piggery wastewaters at high loading rates. *Bioresource Technology*, *100*(19), 4332–4339. doi:10.1016/j.biortech.2009.04.016

Grobbelaar, J. (2000). Physiological and technological considerations for optimising mass algal cultures. *Journal of Applied Phycology*.

Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas. (2009). Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Critical Reviews in Environmental Science and Technology*, *39*(10), 783–842. doi:10.1080/10643380801977610

Huo, H., M. Wang, C. Bloyd and V. Putsche. 2008. Life-cycle assessment of energy use and greenhouse gas emissions of soybean-derived biodiesel and renewable fuels. *Environmental science & technology* 43(3): 750-756.

Ikehata, K. and M. El Din. 2004. Degradation of recalcitrant surfactants in wasterwater by ozonation and advances oxidation processes: A review. *Ozone: science engineering* 26(4): 327-343.

IPAC. (2014). TITLE 35: ENVIRONMENTAL PROTECTION SUBTITLE C: WATER POLLUTION CHAPTER I: POLLUTION CONTROL BOARD, 1–29.

Inoue, S., S. Sawayama, Y. Dote and T. Ogi. 1997. Behaviour of nitrogen during liquefaction of dewatered sewage sludge. *Biomass & Bioenergy* 12(6): 473-475.

Itoh, S., A. Suzuki, T. Nakamura and S. Yokoyama. 1994. Production of heavy oil from sewage-sludge by direct thermochemical liquefaction. *Desalination* 98(1-3): 127-133.

Jena, U. 2011. Effect of operating conditions of thermochemical liquefaction on biocrude production from Spirulina platensis. *Bioresource technology* 102(10): 6221-6229.

Jena, U., N. Vaidyanathan, S. Chinnasamy and K. C. Das. 2011. Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass. *Bioresource technology* 102(3): 3380-3387.

Jones & Stokes. 2003. Evaluation of aeration technology for the Stockton deep water channel. Sacramento, CA. Prepared for the CALFED Bay-Delta Program, Sacramento, CA.

Kallqvist, T. and A. Svenson. 2003. Assessment of ammonia toxicity in tests with the microalga, Nephroselmis pyriformis, Chlorophyta. *Water research* 37(3): 477-484.

Kamjunke, N., B. Köhler, N. Wannicke and J. Tittel. 2008. Algae as Competitors for Glucose with Heterotrophic Bacteria. *Journal of Phycology* 44(3): 616-623.

Kang, J., W. Zhan, D. Li, X. Wang, J. Song and D. Liu. 2011. Integrated catalytic wet air oxidation and biological treatment of wastewater from Vitamin B6 production. *Physics and Chemistry of the Earth* 36(9-11): 455-458.

Kebede-Westhead, E., C. Pizarro, W. W. Mulbry and A. C. Wilkie. 2003. Production and nutrient removal by periphyton grown under different loading rates of anaerobically digested flushed dairy manure. *Journal of Phycology* 39(6): 1275-1282.

Keller, M. D., R. C. Selvin, W. Claus and R. R. L. Guillard. 1987. Media for the culture of oceanic ultraphytoplankton. *J. Phycol.* 23(633): 8.

King, D. L. (1970). The Role of Carbon in Eutrophication on JSTOR. *Journal (Water Pollution Control Federation).*

Kromkamp, J. (1987). Formation and functional significance of storage products in cyanobacteria. *New Zealand Journal of Marine and Freshwater Research*, *21*(3), 457–465. doi:10.1080/00288330.1987.9516241

Kolaczkowski, S. T., P. Plucinski, F. J. Beltran, F. J. Rivas and D. B. McLurgh. 1999. Wet air oxidation: a review of process technologies and aspects in reactor design. *Chemical Engineering Journal* 73(2): 143-160.

Konig, A., H. W. Pearson and S. A. Silva. 1987. Ammonia Toxicity to Algal Growth in Waste Stabilization Ponds. *Water Science and Technology* 19(12): 115-122.

Kumar, A., S. Ergas, X. Yuan, A. Sahu, Q. Zhang, J. Dewulf, F. X. Malcata and H. van Langenhove. 2010. Enhanced CO2 fixation and biofuel production via microalgae: Recent developments and future directions. *Trends in biotechnology* 28(7): 371-380.

Lardon, L., A. Hélias, B. Sialve, J. P. Steyer and O. Bernard. 2009. Life-cycle assessment of biodiesel production from microalgae. *Environmental Science and Technology* 43(17): 6475-6481.

Lau, P. S., N. F. Y. Tam and Y. S. Wong. 1995. Effect of algal density on nutrient removal from primary settled waste-water. *Environmental Pollution* 89(1): 59-66.

Lee, K. M. and P. E. Lim. 2005. Bioregeneration of powdered activated carbon in the treatment of alkyl-substituted phenolic compounds in simultaneous adsorption and biodegradation processes. *Chemosphere* 58(4): 407-416.

Lee, Y., Ding, S., Hoe, C., & Low, C. (1996). Mixotrophic growth ofChlorella sorokiniana in outdoor enclosed photobioreactor. *Journal of Applied Phycology*.

Levec, J. and A. Pintar. 2007. Catalytic wet-air oxidation processes: A review. *Catalysis Today* 124(3-4): 172-184.

Li, Y.-R., Tsai, W.-T., Hsu, Y.-C., Xie, M.-Z., & Chen, J.-J. (2014). ScienceDirect. *Energy Procedia*, *52*, 371–376.

doi:10.1016/j.egypro.2014.07.088
Liao, P. H., Gao, Y., & Lo, K. V. (1993). Chemical precipitation of phosphate and ammonia from swine wastewater. *Biomass and Bioenergy*, 1–7.
Limcaco, C. 2012. Operational energy consumption of Algae Wheel full scale wastewater treatment plant in Reynolds, IN.
Lu, G., C. Wang and X. Guo. 2008. Prediction of toxicity of phenols and anilines to algae by quantitative structure-activity relationship. *Biomedical and Environmental Sciences* 21(3): 193-196.
Lundquist, T. J., I. C. Woertz, N. W. T. Quinn and J. R. Benemann. 2010. A realistic technology and engineering assessment of algae biofuel production. *Energy Biosciences Institute* 1.
Lahav, O. (2000). Bioregenerated ion-exchange process: The effect of the biofilm on ion-exchange capacity and kinetics. *Water Sa*.
Larsdotter, K. (2006). Sammanfattning, 1–50.
Mantzavinos, D., A. G. Livingston, R. Hellenbrand and I. S. Metcalfe. 1996. Wet air oxidation of polyethylene glycols; mechanisms, intermediates and implications for integrated chemical-biological wastewater treatment. *Chemical Engineering Science* 51(18): 4219-4235.
Marker, T., M. Linck and L. Felix. 2010. Integrated Hydropyrolysis and Hydroconversion (IH2) Process for Direct Production of Gasoline and Diesel Fuel from Biomass.
Marker, T. 2005.*Opportunities for biorenewables in oil refineries*.
Marquis, R. E. 1982. Microbioal Barobiology. *Bioscience* 32267-271.
Marquis, R. E. 1976. High-pressure microbila physiology. Volume 14. In *Advances in microbial physiology,* 159-165. ed. J. F. Wilkinson, New York, U.S.: Academic Press Inc.
Mata, T. M., A. A. Martins and N. S. Caetano. 2010. Microalgae for biodiesel production and other applications: A review. *Renewable & Sustainable Energy Reviews* 14(1): 217-232.
Mazumder, D. and A. Dikshit. 2002. Applications of the deep-shaft activated sludge process in wastewater treatment. *International Journal of Environment and Pollution* 17(3): 266-272.
Metcalf & Eddy, G. Tchobanoglous, F. L. Burton and H. D. Stensel. 2003. *Wastewater engineering: treatment and reuse.* 4th ed. Boston: McGraw-Hill.
Minowa, T., S. Yokoyama, M. Kishimoto and T. Okakura. 1995. Oil production from algal cells of Dunaliella tertiolecta by direct thermochemical liquefaction. *Fuel* 74(12): 1735-1738.
Minowa, T. and S. Sawayama. 1999. A novel microalgal system for energy production with nitrogen cycling. *Fuel* 78(10): 1213-1215.
Mata, T. M., Martins, A. A., & Caetano, N. S. (2010). Microalgae for biodiesel production and other applications: A review. *Renewable and Sustainable Energy Reviews*, *14*(1), 217–232. doi:10.1016/j.rser.2009.07.020
Min, M., Hu, B., Mohr, M. J., Shi, A., Ding, J., Sun, Y., et al. (2013). Swine Manure-Based Pilot-Scale Algal Biomass Production System for Fuel Production and Wastewater Treatment—a Case Study. *Applied Biochemistry and Biotechnology*, *172*(3), 1390–1406. doi:10.1007/s12010-013-0603-6

NALBOH. (2010). Understanding Concentrated Animal Feeding Operations and Their Impact on Communities, 1–30.

Nelson, N. O., Mikkelsen, R. L., & Hesterberg, D. L. (2003). Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. *Bioresource Technology*, *89*(3), 229–236. doi:10.1016/S0960-8524(03)00076-2

Órpez, R., Martínez, M. E., Hodaifa, G., Yousfi, El, F., Jbari, N., & Sánchez, S. (2009). Growth of the microalga Botryococcus braunii in secondarily treated sewage. *Desalination*, *246*(1-3), 625–630. doi:10.1016/j.desal.2008.07.016

Pollard, S. J. T., Fowler, G. D., Sollars, C. J., & Perry, R. (1992). Low-cost adsorbents for waste and wastewater treatment: a review. *Science of the Total Environment*, *116*(1-2), 31–52. doi:10.1016/0048-9697(92)90363-W

Roeselers, G., Loosdrecht, M. C. M. V., & Muyzer, G. (2007). Phototrophic biofilms and their potential applications. *Journal of Applied Phycology*, *20*(3), 227–235. doi:10.1007/s10811-007-9223-2

Ruiz-Marin, A., Mendoza-Espinosa, L. G., & Stephenson, T. (2010). Bioresource Technology. *Bioresource Technology*, *101*(1), 58–64. doi:10.1016/j.biortech.2009.02.076

T J Lundquist, I. C. W. N. W. T. Q. A. J. R. B. (2010). A Realistic Technology and Engineering Assessment of Algae Biofuel Production, (12705663), 1–178.

U.S. Environmental Protection Agency. (2008). Municipal Nutient Removal Technologies Reference Document, 1–268.

Ummalyma, S. B., & Sukumaran, R. K. (2014). Cultivation of microalgae in dairy effluent for oil production and removal of organic pollution load. *Bioresource Technology*, *165*, 295–301. doi:10.1016/j.biortech.2014.03.028

Vermette, S., Kanack, J., Bloom, F., Brzezniak, B., Matalonis, W., & Thomas, S. (2014). Sunshine Report: Solar Energy in Western New York, 1–25.

Xian-ping Luo, Hua Lai, Jian-chang Li, Qun Yan, Jun Liu, Dan Feng, & Jun-wen Huang. (2011). Experimental study on adsorption of $NH4^+$ with zeolite's column (pp. 344–348). Presented at the 2011 International Conference on Remote Sensing, Environment and Transportation Engineering (RSETE), IEEE. doi:10.1109/RSETE.2011.5964284

Metcalf & Eddy, Inc. 2003. Wastewater Engineering: Treatment and Reuse. 4th Edition. McGraw-Hill, New York, NY.

National Research Council. 2012. Sustainable Development of Algal Biofuels.

Neilson, A. H. and R. A. Lewin. 1974. The uptake and utilization of organic carbon by algae: an essay in comparative bioghemcistry. *Phycologia* 13(3): 227-264.

Oller, I., S. Malato and J. A. Sánchez-Pérez. 2011. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. *Science of the Total Environment* 409(20): 4141-4166.

Padoley, K. V., P. D. Tembhekar, T. Saratchandra, A. B. Pandit, R. A. Pandey and S. N. Mudliar. 2012. Wet air oxidation as a pretreatment option for selective biodegradability enhancement and biogas generation potential from complex effluent. *Bioresource technology* 120157-164.

Peterson, A., F. Vogel, R. Lachance, M. Froeling and M. Antal. 2008. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environmental Science* 1(1): 32-65.

Pham, M. 2013. Personal communication with Mai Pham about the cytoxicity testing method.

Pham, M., L. Schideman, J. Scott, N. Rajagopalan and M. Plewa. 2013. Chemical and biological characterization of wastewater generated from hydrothermal liquefaction of spirulina. *Environmental science technology* 47(4): 2131-8.

Pope, D. H. and L. R. Berger. 1973. Algal photosynthesis at increased hydrostatic pressure and constant pO2. *Archives of Microbiology* 89(4): 321-325.

Rabus, R. 1995. Anaerobic degradation of ethylbenzene and other aromatic hydrocarbons by new denitrifying bacteria. *Archives of Microbiology* 163(2): 96-103.

Rodolfi, L., G. C. Zittelli, N. Bassi, G. Padovani, N. Biondi, G. Bonini and M. R. Tredici. 2009. Microalgae for oil: strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor. *Biotechnology and bioengineering* 102(1): 100-112.

Rosenberg, J. N., A. Mathias, K. Korth, M. J. Betenbaugh and G. A. Oyler. 2011. Microalgal biomass production and carbon dioxide sequestration from an integrated ethanol biorefinery in Iowa: A technical appraisal and economic feasibility evaluation. *Biomass and Bioenergy* 35(9): 3865-3876.

Schreibe, U. and W. Vidaver. 1973. Photosynthetic energy transfer reversibly inhibited by hydrostatic pressure. *Photochemistry and photobiology* 18(3): 205-208.

Shammas, N. K., L. K. Wang, J. Guild and D. Pollock. 2009. Vertical Shaft Bioreactors. In *Advanced Biological Treatment Processes,* 59-108. ed. L. K. Wang Shammas, N. K. and Hung, Y., Humana Press.

Sheehan, J., T. Dunahay, J. Benemann and P. Roessler. 1998. A Look Back at the U.S. Department of Energy's *Aquatic Species Program: Biodiesel from Algae. NREL/TP-580-24190.*

Sedlak, R., Editor. Phosphorus and Nitrogen Removal from Municipal Wastewater. Principles and Practice. 2nd Edition. 1991

Shoener, B.D.; Bradley, I.; Cusick, R.D.; Guest, J.S. Energy positive domestic wastewater treatment: The roles of anaerobic and phototrophic technologies. Environmental Science: Processes & Impacts, 2014, 16(6): 1204-1222. Invited contribution to Emerging Investigators Special Issue.

Sims, B. 2011. GTI signs licensing agreement with Shell Group subsidiary. Available online at http://biomassmagazine.com/articles/6748/gti-signs-licensing-agreement-with-shell-group-subsidiary/?ref=brm. Accessed April 30 2013.

Smidt, E. and V. Parravicini. 2009. Effect of sewage sludge treatment and additional aerobic post-stabilization revealed by infrared spectroscopy and multivariate data analysis. *Bioresource technology* 100(5): 1775-1780.

Soeder, C., and E. Stengel. 1974. Physiochemical factor affecting metabolism and growth rate. In *Algal Physiology and Biochemistry,* 730. ed. W. D. P. Stewart, Los Angeles, CA: University of California Press.

Speece, R. E. 1983. Anaerobic biotechnology for industrial wastewater treatment. *Environmental science &* technology 17(9): 416A-427A.

Speight, J. G. 2007. The chemistry and technology of petroleum. 114945.

Spaulding, S.A., Lubinski, D.J. and Potapova, M. (2010**).** Diatoms of the United States. http://westerndiatoms.colorado.edu Accessed on 05 December, 2016.

Stalter, D., A. Magdeburg and J. Oehlmann. 2010. Comparative toxicity assessment of ozone and activated carbon treated sewage effluents using an in vivo test battery. Water research 44(8): 2610-2620.

Suárez-Ojeda, M. E., J. Carrera, I. S. Metcalfe and J. Font. 2008. Wet air oxidation (WAO) as a precursor to biological treatment of substituted phenols: Refractory nature of the WAO intermediates. *Chemical Engineering Journal* 144(2): 205-212.

Suzuki, A., T. Nakamura, S. Yokoyama, T. Ogi and K. Koguchi. 1988. Conversion of Sewage-Sludge to Heavy Oil by Direct Thermochemical Liquefaction. *Journal of Chemical Engineering of Japan* 21(3): 288-293.

Tam, N. F. Y. and Y. S. Wong. 1996. Effect of ammonia concentrations on growth of Chlorella vulgaris and nitrogen removal from media. *Bioresource technology* 57(1): 45-50.

Tchobanoglous, G., F. L. Burton and Metcalf & Eddy. 1991. *Wastewater engineering: treatment, disposal, and reuse.* 3rd ed. New York: McGraw-Hill.

Torri, C., L. Alba, C. Samori and D. Fabbri. 2012. Hydrothermal Treatment (HTT) of Microalgae: Detailed Molecular Characterization of HTT Oil in View of HTT Mechanism Elucidation. *Energy fuels* 26(1): 658-671.

U.S. DOE. 2010. National algal biofuels technology roadmap.

U.S. DOE. 2008. Waste Heat Recovery: Techonology and Opportunities in U.S. Industry.

U.S. DOE. 2006. Biodiesel handling and use guidelines, third edition. DOE/GO-102006-2358.

U.S. EIA. 2012. Annual Energy Review 2011.

Environmental Protection Agency. (2001). Environmental assessment of proposed revisions to the national pollutant discharge elimination system regulation and the effluent guidelines for concentrated animal feeding operations. Available from http://cfpub.epa.gov/npdes/docs.cfm?view=archivedprog&program_id=7&sort=name

Oswald, with H.B. Gotaas, H.F. Ludwig and V. Lynch. , (January 1953). "Algae Symbiosis in Oxidation Ponds. II. Growth Characteristics of Chlorella pyrenoidosa Cultured in Sewage," Reprinted in Sewage and Industrial Wastes 25:1

Oswald, W.J., 1988. Micro-algae and wastewater treatment. In: Borowitzka, M.A., Borowitzka, L.J. (Eds.), Micro-algal Biotechnology, Cambridge Univ. Press, pp. 305–328.

U.S. EPA. 2011. Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2010. EPA-530-F-11-005.

U.S. EPA. 2006. Energy Conservation-Wastewater Management Factsheet.

U.S. EPA, Office of Wastewater Management. 2006. Emerging Technologies for Biosolids Management. EPA 832-R-06-005.

USDA. 2011. Agricultural Statistics 2011.

USDA. 1995. Animal Manure Management, RCA Issue Brief #7. USDA. Available at: http://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/technical/nra/rca/?&cid=nrcs143_014211. Accessed 11/20 2012.

Vardon, D. R., B. K. Sharma, G. V. Blazina, K. Rajagopalan and T. J. Strathmann. 2012. Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis. *Bioresource technology* 109178-187.

Vardon, D., B. K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang and T. J. Strathmann. 2011. Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge. *Bioresource technology* 102(17): 8295-8303.

Wang, L., Y. Li, P. Chen, M. Min, Y. Chen, J. Zhu and R. R. Ruan. 2010. Anaerobic digested dairy manure as a nutrient supplement for cultivation of oil-rich green microalgae Chlorella sp. *Bioresource technology* 101(8): 2623-2628.

Wang, M. Q., J. Han, Z. Haq, W. E. Tyner, M. Wu and A. Elgowainy. 2011. Energy and greenhouse gas emission effects of corn and cellulosic ethanol with technology improvements and land use changes. *Biomass and Bioenergy* 35(5): 1885-1896.

WERF. 2011. Energy production and efficiency research-the roadmap to net-zero energy.

Williams, P. J. L. B. and L. M. L. Laurens. 2010. Microalgae as biodiesel biomass feedstocks: Review analysis of the biochemistry, energetics economics. *Energy Environmental science* 3(5): 554.

Xu, L. 2011. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresource technology* 102(8): 5113-5122.

Yang, J., M. Xue, X. Zhang, Q. Hu, M. Sommerfeld and Y. Chen. 2011. Life-cycle analysis on biodiesel production from microalgae: Water footprint and nutrients balance. *Bioresource technology* 102(1): 159.

Yokayama, S., A. Suzuki, M. Murakami, T. Ogi, K. Koguchi and E. Nakamura. 1987. Liquid fuel production from sewage-sludge by catalytic vonversion using sodium-carbonate. *Fuel* 66(8): 1150-1155.

Yokoyama, S., A. Suzuki, M. Murakami, T. Ogi, K. Koguchi and E. Nakamura. 1987. Liquid fuel production from sewage-sludge by catalytic conversion using sodium-carbonate. *Fuel* 66(8): 1150-1155.

Yu, G., Y. Zhang, L. C. Schideman, T. Funk and Z. Wang. 2011. Hydrothermal liquefaction of low lipid content microalgae into bio-crude oil. *Transactions of the ASABE* 54(1): 239.

Yu, G. 2012. Hydrothermal liquefaction of low-lipid microalgae to produce bio-crude oil. PhD diss. University of Illinois at Urbana-Champaign.

Yu, G., Y. Zhang, L. Schideman, T. Funk and Z. Wang. 2011. Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae. *Energy Environmental Science* 4(11): 4587-4595.

Zhou, Y. and Schideman, L.C., Yu, G., Zhang,Y. In revision. Environment-Enhancing Energy: A synergistic combination of algal wastewater treatment and biofuel production maximized by nutrient and carbon recycling. *Energy Environ. Sci.*

Zhou, Y., L. C. Schideman, Y. Zhang and G. Yu. 2011. Environment-Enhancing Energy: A Novel Wastewater Treatment System that Maximizes Algal Biofuel Production and Minimizes Greenhouse Gas Emissions. In Los Angeles, CA: WEFTEC 2011.

Zhou, D., L. Zhang, S. Zhang, H. Fu and J. Chen. 2010. Hydrothermal Liquefaction of Macroalgae Enteromorpha prolifera to Bio-oil. *Energy fuels* 24(7): 4054-4061.

Zhou, Y. 2010. Improving algal biofuel production through nutrient recycling and characterization of photosynthetic anomalies in mutant algae species. PhD diss. Urbana, IL: University of Illinois at Urbana-Champaign.

ZoBell, C. E. 1970. Pressure effects on morphology and life processes of bacteria. In *High pressure effects on cellular processes,* 85-130. ed. A. M. Zimmerman, New York: Academic Press.

APPENDIX A: MASS BALANCE PARAMETERS

Wastewater			
Parameter	**Units**	**Value**	**Data Sources**
HRT	day	1	This study
Flow	m3/d	500000	Calculation
BOD	mg/L	200	Metcalf and Eddy, 2003
TN	mg/L	35	Metcalf and Eddy, 2003
TOC:BOD		0.72	Metcalf and Eddy, 2003
C	ton/day		Calculation
N	ton/day		Calculation
Primary Clarifier			
Parameter	**Units**	**Value**	**Data Sources**
BOD removal	%	40	Lunquist et al., 2010
Sludge to BOD ratio		0.39	This study (Ch 4)
Settled sludge solid content	%	1	Ross et al., 2008
Sludge C content	%	45	This study
Sludge N content	%	5	This study
Algaewheel System			
Parameter	**Units**	**Value**	**Data Sources**
total Surface area	hectare	100	Assumed
Depth of the system	m	0.5	Assumed
Evaporation	inch/day	0.2	Bordovsky et al.,1998
Biomass productivity (with adsorbent)	g/m2	28	This study (Ch 5)
Biomass productivity (without adsorbent)	g/m2	26	This study (Ch 5)
Biomass C content	%	45	This study (Ch 5)
Biomass N content	%	5	This study (Ch 5)
Effluent BOD	mg/L	24	This study (Ch 5), assumed
High Rate Pond			
Parameter	**Units**	**Value**	**Data Sources**
total Surface area	hectare	100	Assumed
Depth of the system	m	0.3	Lunquist et al., 2010
Evaporation	inch/day	0.2	Bordovsky et al.,1998
Biomass productivity (with adsorbent)	g/m2	22	Lunquist et al., 2010
Biomass C content	%	45	This study
Biomass N content	%	5	This study
Effluent BOD	mg/L	24	Lunquist et al., 2010
Secondary Clarifier			
Parameter	**Units**	**Value**	**Data Sources**
BOD removal	%	40	Lunquist et al., 2010
Settled sludge solid content	%	1	Ross et al., 2008
Biomass C content	%	45	This study
Biomass N content	%	5	This study

Gravity Thickener			
Parameter	**Units**	**Value**	**Data Sources**
Harvest efficiency	%	95	Lunquist et al., 2010
Solid content after thickener	%	3	Assumed
Biomass C content	%	45	This study
Biomass N content	%	5	This study
Drying Bed			
Parameter	**Units**	**Value**	**Data Sources**
Solid content after drying (HTL route)	%	20	Assumed
Solid content after drying (extraction route)	%	80	Lunquist et al., 2010
HTL			
Parameter	**Units**	**Value**	**Data Sources**
HTL crude oil yield	%	35	This study
C recovery in crude oil	(C-oil/C-feedstock)%	60	This study
N recovery in crude oil	(N-oil/N-feedstock)%	36	This study
Oil Extraction			
Parameter	**Units**	**Value**	**Data Sources**
Oil content in algae	%	25	Lunquist et al., 2010
Extraction efficiency	%	98	Lunquist et al., 2010
C content in algae oil	%	50	Lunquist et al., 2010
CHG			
Parameter	**Units**	**Value**	**Data Sources**
Biogas yield	% carbon to gass	55	Jones et al., 2014
Methane content in biogas	%	70	Jones et al., 2014
Heating value of methane	MJ/m3	39	EIA, 2000
Anaerobic Digestion			
Parameter	**Units**	**Value**	**Data Sources**
Biogas yield	L/g-biomass	0.3	Lunquist et al., 2010
Methane content in biogas	%	70	Lunquist et al., 2010
Heating value of methane	MJ/m3	39	EIA, 2000
CHP			
Parameter	**Units**	**Value**	**Data Sources**
Electricity conversion efficiency	%	40	EIA, 2016
Thermal conversion efficiency	%	40	EIA, 2016

APPENDIX B: ECONOMIC COST ASSUMPTION AND ESTIMATION

Major Capital Cost for Scenario 1 (Ads-Algaewheel®/HTL)

Item	Source scale		Source cost		Source year	Project scale		Project year	n	Item Cost	Note	Source
Land	120	ha	30,000	$/ha	2010	120	ha	2016	1	5,473,418		Lunquist et al., 2010
1. Clarifier			3.45	$/ft2	1969	54,000	ft2	2016	1	1,177,009	HRT 1 hr for 500 MGD, Concrete wall, 4.2m depth	Lunquist et al., 2010
Algae Cultivation System			30	$/m2	2016	100	ha	2016	1	30,000,000		Personal comminication, estimate
Aerator			17	$/lb O2 Blower	1991	6,715	lb O2/hr	2016	1	5,930,062		Sedlak R. 1991
			9.5	$/lb O2/d diffuser system	1991	6,715	lb O2/hr					
2. Clarifier			3.45	$/ft2	1969	108,000	ft2	2016	1	2,354,018	HRT 2 hr for 500 MGD, Concrete wall, 4.2m depth	Lunquist et al., 2010
Thickeners	22	ton	256,000	$	2010	41.42	ton	2016	0.7	606,104		Lunquist et al., 2010
Drying beds	670	m3	2,420,000	$	2010	1,174	m3	2016	0.7	5,448,623		Lunquist et al., 2010
Water piping	62	MLD	1,660,000	$	2010	500	MLD	2016	0.7	5,240,426		Lunquist et al., 2010
HTL	100	Dry ton	20,000,000	$	2014	41.42	ton	2016	1	8,745,121		Jones et al., 2014
Electrical	120	ha	1,900,000	$	2016	120	ha	2016	1	2,888,748		Lunquist et al., 2010
Buildings	120	ha	120,000	$	2010	120	ha	2016	1	182,447	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Silo storage	120	ha	109,000	$	2010	120	ha	2016	1	165,723	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Vehicles	120	ha	100,000	$	2010	120	ha	2016	1	152,039	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Road and Fencing	120	ha	338,000	$	2010	120	ha	2016	1	513,893	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Adsorbent (EAC,zeolite)			600	$/ton	2016	3,000	ton	2016	1	1,800,000		Alibaba, 2016

Major Capital Cost for Scenario 2 (Algaewheel®/HTL/CHG)

Item	Source scale		Source cost		Source year	Project scale		Project year	n	Item Cost	Note	Source
Land	120	ha	30,000	$/ha	2010	120	ha	2016	1	5,473,418		Lunquist et al., 2010
1. Clarifier			3.45	$/ft2	1969	54,000	ft2	2016	1	1,177,009	HRT 1 hr for 500 MGD, Concrete wall, 4.2m depth	Lunquist et al., 2010
Algae Cultivation System			30	$/m2	2016	100	ha	2016	1	30,000,000		Personal comminication, estimate
Aerator			17	$/lb O2 Blower	1991	6,715	lb O2/hr	2016	1	5,930,062		Sedlak R. 1991
			9.5	$/lb O2/d diffuser system	1991	6,715	lb O2/hr					
2. Clarifier			3.45	$/ft2	1969	108,000	ft2	2016	1	2,354,018	HRT 2 hr for 500 MGD, Concrete wall, 4.2m depth	Lunquist et al., 2010
Thickeners	22	ton	256,000	$	2010	39.52	ton	2016	0.7	586,505		Lunquist et al., 2010
Drying beds	670	m3	2,420,000	$	2010	1,174	m3	2016	0.7	5,448,623		Lunquist et al., 2010
Water piping	62	MLD	1,660,000	$	2010	500	MLD	2016	0.7	5,240,426		Lunquist et al., 2010
HTL	100	Dry ton	20,000,000	$	2014	39.52	ton	2016	1	8,343,969		Jones et al., 2014
Electrical	120	ha	1,900,000	$	2016	120	ha	2016	1	2,888,748		Lunquist et al., 2010
Buildings	120	ha	120,000	$	2010	120	ha	2016	1	182,447	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Silo storage	120	ha	109,000	$	2010	120	ha	2016	1	165,723	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Vehicles	120	ha	100,000	$	2010	120	ha	2016	1	152,039	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Road and Fencing	120	ha	338,000	$	2010	120	ha	2016	1	513,893	Split costs into half for cultivation and conversion	Lunquist et al., 2010
CHG	100	ton	9,100,000	$	2016	40	ton	2016	1	3,596,320		Snowden-Swen et al., 2016
Biogas Turbine	3165	m3	2,040,000	$	2010	2,608	m3	2016	1	2,555,760		Lunquist et al., 2010

Major Capital Cost for Scenario 3 (HRP/Transesterification/Anaerobic Digestion)

Item	Source scale		Source cost		Source year	Project scale		Project year	n	Item Cost	Note	Source
Land	120	ha	30,000	$/ha	2010	120	ha	2016	1	5,473,418		Lunquist et al., 2010
1. Clarifier	62	MLD	420000	$	2010	62	MLD	2016	1	638,565		Lunquist et al., 2010
Algae Cultivation System	100	ha	3410000	$	2010	100	ha	2016	1	5,184,543		Lunquist et al., 2010
CO2 Delivery	100	ha	594000	$	2010	100	ha	2016	1	903,114		Lunquist et al., 2010
2. Clarifier	62	MLD	948000	$	2010	62	MLD	2016	1	1,441,333		Lunquist et al., 2010
Thickeners	22	ton	256,000	$	2010	22.00	ton	2016	1	389,221		Lunquist et al., 2010
Drying beds	670	m3	2,420,000	$	2010	670	m3	2016	1	3,679,353		Lunquist et al., 2010
Water piping	62	MLD	1,660,000	$	2010	62	MLD	2016	1	2,523,854		Lunquist et al., 2010
Flash Dryer	22	ton	20,000,000	$	2010	39.52	ton	2016	1	37,927,131		Lunquist et al., 2010
Extraction plant share	22	ton	2,430,000	$	2010	22.00	ton	2016	1	3,694,557		Lunquist et al., 2010
Electrical	120	ha	1,900,000	$	2010	120	ha	2016	1	2,888,748		Lunquist et al., 2010
Buildings	120	ha	120,000	$	2010	120	ha	2016	1	182,447	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Silo storage	120	ha	109,000	$	2010	120	ha	2016	1	165,723	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Vehicles	120	ha	100,000	$	2010	120	ha	2016	1	152,039	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Road and Fencing	120	ha	338,000	$	2010	120	ha	2016	1	513,893	Split costs into half for cultivation and conversion	Lunquist et al., 2010
Anaerobid Digestor	22	ton	2,440,000	$	2010	22	ton	2016	1	3,709,761		Lunquist et al., 2010
Biogas Turbine	3165	m3	2,040,000	$	2010	3,165	m3	2016	1	3,101,603		Lunquist et al., 2010

Annual Administration and Labor Costs

Admin Costs	$/yr
Plant Manager	114,000
Supervisor of Operators	93,600
Lab Manager	62,400
Admin/Secretary	17,700
Total Admin Salaries	288,000
Benefits @!30%	86,400
Total Admin costs	$375,000

Operators Cost	$/yr
Avearge Operator Salary	41,100
Number of Operators	14
Total Operator Salaries	575,000
Benefits @ 30%	173,000
Total Operator Costs $	748,000