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Nutrient Removal & Greenhouse Gas Abatement with CO₂ Supplemented Algal High Rate Ponds

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ABSTRACT

High rate algae ponds fed clarified domestic wastewater and CO2-rich flue gas are expected to remove nutrients to concentrations similar to those achieved in mechanical treatment technologies, such as activated sludge. However, the energy intensity of wastewater treatment with CO2-supplemented high rate ponds (HRPs) would be less than that of mechanical treatments. In conjunction with anaerobic digestion of algal biomass and co-substrates, the algae-based system would produce a substantial excess of electricity. Greenhouse gas abatement from such CO2-HRP/digestion systems would stem mainly from energy conservation and the offset of fossil fuel electricity with biogas-derived electricity. Laboratory experiments showed nutrient removals of >98% for ammonium and >96% for phosphorus with mixed culture microalgae grown on CO₂-supplemented primary wastewater effluent. An engineering numerical model for CO2-HRP/digestion facilities (based in part on large-scale algae production under southern California conditions) indicates a potential energy surplus of 330 kWh/ML (1,200 kWh/MG) from biogas-derived electricity, compared to the net energy consumption of about 760 kWh/ML (2,900 kWh/MG) at typical activated sludge facilities with nitrification/denitrification. Considering the net electricity production and energy savings of the CO₂-HRP/digestion systems, a greenhouse gas abatement potential of 660 kg CO_{2ea}/ML (2,500 kg CO_{2eo}/MG) treated is expected for a 100-ha facility treating 20 MGD.

KEYWORDS: Algae, Ponds, Wastewater treatment, Nutrient removal, Greenhouse gas, CO2

INTRODUCTION

Publicly-owned wastewater treatment plants in the U.S. consume an estimated 21 billion kilowatt hours (kWh) per year (EPRI 2002). This electricity consumption is equivalent to 12.7 million metric tons of CO₂ emitted per year, based on the U.S. EPA estimated national average of 0.603 kg CO₂/kWh delivered (EPA 2009). Imported power for mechanical aeration of wastewater is the dominant source of greenhouse-gas emissions at wastewater treatment facilities (WERF 2009). Conventional activated sludge wastewater treatment facilities consume more energy than they can recover through anaerobic digestion of sludge. The addition of Biological Nutrient Removal (BNR) technologies such as nitrification/denitrification increases the energy consumption by about an additional 400 kWh/ML (1,500 kWh/MG) (Owen 1982). Algae-based

wastewater treatment offers an alternative to mechanically based wastewater treatment and can deliver simultaneous nutrient removal and CO₂ abatement.

Algal-based wastewater treatment

The late William Oswald of the University of California was a leading proponent of microalgal based wastewater treatment and is credited with the basic model describing the algal-bacterial interactions in wastewater treatment ponds, shown in Figure 1. The simplified relationship is that aerobic bacteria consume organics found in wastewater and create the byproducts of CO_2 and soluble nutrients such as N and P. These byproducts and wastewater CO_2 , N, and P are then consumed by photoautotrophic microalgae that in turn release O_2 as a byproduct. The oxygen promotes the removal of biochemical oxygen demand.. The main advantage of this type of system is that energy is provided by the sun which drives algal photosynthesis, thus decreasing the need for electrical-driven compressors to provide oxygen to the bacteria.





Today there are up to 8,200 wastewater facilities in the U.S. with conventional treatment ponds (USEPA 2000). At conservatively-designed wastewater pond facilities, mechanical aeration requirements are minimal, and while the performance of conventional ponds has been satisfactory for BOD removal in many cases, the ponds are limited in their ability to remove nutrients and effluent total suspended solids concentrations are often high due to suspended algae.

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Algal High Rate Ponds

Algal high rate ponds (HRPs) were developed beginning in the 1950s as an alternative to unmixed oxidation ponds for BOD, suspended solids, and pathogen removal. HRPs have been designed to be shallow (30-100 cm) with a raceway shape and include a large paddle wheel vane pump to create a channel velocity sufficient for gentle mixing (Figure 2). Use of facultative ponds for initial treatment prior to HRPs has been advocated and implemented in a few places (Oswald 1990). With sufficient hydraulic residence time, depending on climate and load, these systems remove soluble BOD to low-levels, but effluent total suspended solids concentrations have often been high due to unsettled algae (e.g., 111 mg/L TSS, Green et al. 1995). However, assimilation of dissolved nutrients has been an ancillary concurrent benefit of these systems. Ammonium and phosphate removal efficiencies of 89% and 49%, respectively, have been measured in facultative-HRP sequences (Green et al. 1995). However, hydraulic residence times in the HRPs of 7-13 days were used. This low rate of nutrient assimilation was likely due to inorganic carbon limitation on algal growth, as indicated by mean morning pH measurements of 8-10 (Green et al. 1996).



Depth = 30 cm

Figure 2: Simplified Algal High Rate Pond Plan View Schematic

Algae growth in CO₂-supplemented HRPs is not limited by inorganic carbon concentrations, which promotes accelerated algae growth and complete assimilation of dissolve nutrients. Removal of the resulting algae from the effluent flow is ideally accomplished by bioflocculation of the algae, followed by sedimentation to create an effluent low in TSS. Bioflocculation has been demonstrated for periods of weeks to months by several workers (e.g., Benemann et al. 1980, Cal Poly unpublished). Thus, CO₂-supplemented HRPs for wastewater treatment have several advantages over conventional wastewater treatment but also disadvantages (Table 1). Some of the advantages include short retention times (3-5 days) compared to conventional ponds (>10 days), minimal mixing energy requirements, and the potential for high BOD and nutrient removals. Production of algal biomass is an advantage if there is a use for the biomass such as biofuel production or fertilizer, biofuel and fertilizer production could have both economic and CO_2 abatement benefits. Disadvantages include increased solids handling, seasonality of algae growth, high land use, and a short track record for bioflocculation/settling of algae to meet

discharge limits and harvest the biomass.

Advantages	Disadvantages
Increased biomass production for biofuel and fertilizer	Increased biomass production with increased handling effort
Short retention time compared to conventional ponds	More experience with bioflocculation and settling of algal biomass is needed
Minimal energy requirements compared to mechanical treatment	Seasonality of treatment
CO ₂ abatement via biofuel production and recycling of algae nutrients as fertilizer	Large land requirements

Table 1: Algal High Rate Pond Advantages and Disadvantages.

Nutrient Removal and CO₂ Abatement

The potential of CO2-supplemented HRPs was explored via laboratory experiments and a techno-economic/CO2 abatement model. Microalgae assimilate carbon, nitrogen, and phosphorus for cell growth. Algae grown on municipal wastewater in high rate ponds can be carbon limited due to the low C:N:P ratio of municipal wastewater (about 20:8:1) relative to that of microalgae (about 50:8:1). This carbon deficiency contributes to slow algae growth and incomplete nutrient removal. By supplementing CO₂ into the wastewater from an alternative waste source, such as on-site flue gas, this deficiency can be overcome. To explore the limit of simultaneous nitrogen and phosphorus assimilation by CO₂ supplemented, wastewater-grown algae and the relationship between intracellular N:P ratios and wastewater media N:P were studied in the laboratory at Cal Poly State University, San Luis Obispo during Fall 2007 to Spring 2008.

Additionally, a Microsoft[®] Excel[®]-based computer model was developed to determine the potential greenhouse gas (GHG) abatement for a large (20 MGD) wastewater treatment facility implementing CO₂-supplemented algal high rate ponds. Three potential areas of abatement were analyzed: increased energy efficiency over conventional wastewater treatment and renewable energy production from anaerobic digestion of algae with co-substrates.

METHODOLOGY

Nutrient Removal

Mixed cultures (polycultures) microalgae, commonly found in wastewater, were grown in diluted wastewater media containing N:P mass ratios ranging from 2.5:1 to 60:1 (Fulton 2009). The simultaneous removal of both N and P was monitored, in addition to the N and P content of the biomass grown. The study was conducted using 1-L Roux bottles as the growth vessels with

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full-spectrum fluorescent lighting on a 16 h-On:8 h-Off cycle. The bottles were continuously sparged with an air-CO₂ mixture and operated with a 3-day hydraulic residence time. Two sets of municipal wastewater media were collected, separated by several months, and used in experiments designated "A" and "B." The wastewater was collected from the primary effluent weir channel at the San Luis Obispo municipal wastewater treatment plant. The undiluted primary wastewater characteristic are shown in Table 3. To prevent light limitation from affecting the results, the wastewater had to be diluted to achieve target cell concentrations of less than 600 mg/L TSS. The wastewater feed was mixed with a defined media containing N or P added to achieve the desired N:P ratio. Analytical analysis included soluble chemical oxygen demand (sCOD), TSS, volatile suspended solids (VSS), total ammonia (NH_x), total Kjeldahl nitrogen (TKN), and total phosphorus (TP).

Total ammonia $(NH_3+NH_4^+, \text{ or } NH_x)$ concentrations were determined using the Ammonia-Selective Electrode Method (APHA, 1995; Appendix A), and by a fluorometric method, Protocol B (Holmes *et al.* 1999). Both nitrite (NO_2^-) and nitrate (NO_3^-) were determined by ion chromatography (Dionex DX 120). Organic nitrogen was measured to estimate the N content of the algal cells using the Macro-Kjeldahl Method (APHA, 1995). Both dissolved reactive phosphorus (DRP) and total phosphorus (TP) were measured by the Ascorbic Acid Method (APHA 1995).

	Wastewater used in Experiments A	Wastewater used in Experiment B	
sCOD (mg/L)	174	96	
TSS (mg/L)	87	98	
VSS (mg/L)	45	87	
NH _x (mg/L as N)	38	32	
TKN (mg/L as N)	56	63	
TP (mg/L as P)	2.8	6.5	

Table 2: Characteristics of primary treated wastewater used in Experiments A and B.

The micronutrient and macronutrient solutions for the defined media of Experiments A and B were based on algal growth potential medium (APHA, 1995). In all experiments, NH_4Cl was substituted for NaNO₃ in the media, as oxidized nitrogen is typically absent from domestic wastewater. K₂HPO₄ was the form of phosphorus used in all media (APHA, 1995; Andersen, 2005). Table 3 shows the final conditions in the feed for the experiments.

N:P Mass ratio in feed	Total N in feed (mg/L as N)	NH _x in feed (mg/L as N)	Total P in feed (mg/L as P)	Experiment
2.5	14.0	3.5	5.6	В
5	14.0	9.5	2.8	А
20	14.0	9.5	0.7	А
20	14.0	3.5	0.7	В
30	21.0	16.5	0.7	А
60	42.0	38.6	0.7	В

Table 3: N:P feed ratios for all experiments.

CO₂ Abatement Model

In order to determine theoretical potential CO₂ abatement with algal high rate ponds, an engineering model was developed for a hypothetical 20 MGD facility located in southern California. The modeled facility consists of primary sedimentation followed by 25 4-ha algal high rate ponds, operated in parallel, making the total pond footprint equal to 100 ha. The ponds receive a wastewater flow of 20 MGD and operate on a hydraulic retention time of 4 days. The keystone of the model is the assumed annual algae productivity of 20 g/m²/day, which is the generally accepted average productivity for the southern US (ABS 2008). Hourly and monthly productivity assumptions were made based on previous in-house research. System design based on hourly production of algae biomass allows for an accurate analysis for the infrastructural requirements such as pipe diameters required for pumping of harvested algae biomass during peak production. Estimated national average energy requirements were assumed for the influent lift station, headworks, and effluent disinfection.

Gas spargers placed in the bottom of the ponds deliver flue gas that has been captured from onsite electrical generation as well as minimal imported sources. Carbon dioxide from the breakdown of organics in the wastewater was also considered. A biochemical oxygen demand (BOD) breakdown factor of 1.2 g CO₂ produced/ g BOD was used (based on a wastewater organic matter stoichiometry of C₆H₁₁ON₂). To simplify the model, nutrients including carbon, are considered non-limiting, and productivity is controlled by insolation and temperature.

Energy consumption for pumping, mixing, flue gas distribution, and sedimentation harvesting were all considered. Harvesting efficiencies were assumed similar to that of activated sludge as confirmed by in-house experiments. All harvested algal biomass is combined with an imported, concentrated carbon, co-substrate waste and anaerobically digested. Co-substrate carbon waste is added to increase the C:N ratio and improve the digestion efficiency of algae, as demonstrated by Yen and Brune (2007).

RESULTS

Nutrient Removal Results

The indoor experiments showed that nutrient removal was nearly complete for all cases supplemented with CO_2 . NH_x removal was >98%, and dissolved P removal was >96%. Total ammonia residual in the effluent from the multiple N:P feed ratio experiments were all under 0.1 mg/L as N, except for the culture that was fed a 60:1 N:P ratio which had a effluent concentration of <0.5 mg/L as N (Figure 3). The total dissolved reactive phosphorus residual was all <0.025 mg/L as P (Figure 4). There was no detectible pattern for the residual phosphorus, but all the residual concentrations are low. The results for both the N and P effluent residual show that even at a retention time of three days, algae can assimilate both nitrogen and phosphorus, leaving almost non-detectible nutrient levels with the supplementation of CO₂.



Figure 3: Total ammonia residual in the effluent of laboratory wastewater algae cultures (Fulton 2009).



Figure 4: Dissolved Reactive phosphorus residual in the effluent of laboratory wastewater algae cultures (Fulton 2009).

The ability of algae to assimilate almost all soluble N and P simultaneously over a wide range of media N:P ratio is due to the flexible stoichiometry of algal cells. In fact, algal cells appear to equilibrate with the N:P ratio in the media. Cell N and P concentrations were found to be proportional to the N:P ratio in wastewater (Figure 5). This ability of algae to assimilate almost all nutrients even in media with extreme nutrient ratios indicates that a wide variety of wastewaters could be treated with CO₂-supplemented high rate ponds.



Figure 5: The linear relationship between N:P ratio in feed to N:P ratio assimilated by cells (Fulton 2009).

CO₂ Abatement Model Results

On-site energy consumption for a 76 MLD (20 MGD) algal high rate pond facility is estimated to average on an annual basis about 230 kWh/ML (880 kWh/MG) treated. This electricity consumption is substantially less than the average energy consumption for an Activated Sludge Facility (ASF), which ranges from 340 to 660 kWh/ML (1,300 to 2,500 kWh/MG) depending on wastewater flow. However, basic activated sludge operations for secondary treatment do not obtain complete nutrient removal, and algal high rate ponds should be compared to a more advanced treatment technology. The difference in the comparison of energy consumed becomes even greater when compared to an activated sludge facility that is implementing Biological Nutrient Removal (ASF/BNR), which can consume between 740 and 1,000 kWh/ML (2,800 and 4,000 kWh/MG). On-site energy production must also be factored into the overall energy balance. At conventional wastewater treatment facilities, anaerobic digestion of sludge produces an average $28 \text{ m}^3/10^3$ persons d (Metcalf and Eddy 2003). However, most treatment plants in the US do not produce or use biogas. Only fifteen percent of the total wastewater flow in the U.S. is treated at facilities that use biogas from anaerobic digestion (Chaudhry 2005). When biogas is produced and used, it could offset 50% of the energy demand for an ASF as a best case scenario (Figure 6). The average net energy deficient, which includes on-site biogas production, for an ASF and an ASFw/BNR treatment system is equal to 370 and 770 kWh/ML (1,400 and 2,900 kWh/MG), respectively (Figure 6). For the Algal High Rate Ponds there is an average net gain in energy of 330 kWh/ML (1,240 kWh/MG) that is produced from the anaerobic digestion of primary sludge, algal biomass, and additional co-substrate (Figure 6). This available energy produced varies depending on seasonality and associated algae growth.



Figure 6: Energy consumption and on-site production from anaerobic digestion.

**Activated sludge biogas and energy production assumptions: 23m³biogas/1000 cap/d, 100 gallons ww/cap/d, 20 MGD facility, 22,400 kJ/m³ lower heating value of biogas, 30% engine efficiency.

 CO_2 Abatement can be calculated for the Algal High Rate Ponds from the energy savings shown in the previous graph. The conventional wastewater treatment systems energy requirements were multiplied by the national average of 0.603 kg CO_2 released/kWh delivered (EPA 2009a) to give a total of 220 and 550 kg CO_2 released/ML (830 and 1,700 kg CO_2 /MG) for the ASF and the ASFw/BNR respectively (Figure 7). Algal High Rate Ponds supplemented with CO_2 can acheive, effectively, the same treatment as ASFw/BNR and still produce excess energy on yearly average. Therefore, the CO_2 abatement for the Algal High Rate Ponds is the equivalent of what the ASFw/BNR would have emitted in its place at 460 kg CO_2/ML (1,700 kg CO_2/MG) plus the excess renewable energy produced equvilent CO_2 offset at 200 kg CO_2/ML (750 kg CO_2/MG) to make a total abatement of 660 kg CO_2/ML (2,500 kg CO_2/MG) (Figure 7). Using the produced sludge and captured nutrients as fertilizer would also create CO_2 abatement. However, this is not considered here as it would be difficult to compare to conventional wastewater sludge. The additional CO_2 imported and biofixated, i.e. not met from onsite flue gas, could be counted as an additional abatement with an estimated 26 kg CO_2/ML (100 kg CO_2/MG) annual average imported.



Figure 7: CO₂ production from conventional wastewater treatment facilities compared to Algal High Rate Ponds and their net energy production.

DISCUSSION/CONCLUSIONS

Algal cultures were found to be flexible in their ability to treatment wastewaters with a variety of N:P ratios, which allowed them to remove both dissolved N and P to low levels, while growing a large amount of biomass.. These results indicate that CO₂-enriched pond systems would be useful in removing nutrients from domestic wastewater and wastewaters from industry and agriculture with a wide range of N:P ratios, while reducing CO₂ emissions relative to mechanical treatment technologies. The greenhouse gas abatement potential of a full-scale Algal High Rate Pond Facility (660 kg CO₂/ML or 2,500 kg CO₂/MG) is substantial compared to a typical ASFw/BNR. The majority of these CO₂ savings are from the energy efficiency gain by using a photosynthetic based wastewater treatment and anaerobic digestion. Currently small-scale experiments on algae ponds with areas of 3 m² each are being conducted to confirm assumptions

made in the engineering model. A pilot-scale facility is also in the planning process to demonstrate CO_2 supplemented Algal High Rate Ponds on a larger scale.

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