

ElectroConcentration and ElectroFlotation for Dewatering/Water Purification

Maria Inman^a, EJ Taylor^a, Heather McCrabb^a, Brian Skinn^a, Joseph Kell^a, Ben Stuart^b

^aFaraday Technology, Inc., 315 Huls Drive, Clayton, OH 45315

^bOhio University, Athens, OH 45701

Faraday Technology is developing a novel process that enables dewatering of bioalgae containing solutions, and has applicability to water purification through removal of particulate species. The technology is being developed through a project that is investigating concentration of microalgae prior to the extraction of lipids for oil production. Initial results show that the FARADAYICSM ElectroConcentration Process is capable of concentrating algae from ~ 7 g/L to ~82 g/L while depleting the treated area to ~ 2 g/L. In addition, the electrochemical algae separation technique results in floating “mats” of algae that can be readily skimmed off of the surface of the treated solution. This technology may be applicable to dewatering of algae in saltwater environments, as well as freshwater. Future results will explore the effects of pulsed fields and cell design on the separation energy efficiency of the process in preparation for scaling up to continuous processing

Introduction

There are many opportunities for application of water and/or biomass recovery using dewatering/concentration techniques, including wastewater treatment, reservoir algae control, lake cleanup, membrane separation, pharma/nutraceutical manufacturing, and algae separation for biofuel production. This latter application is the focus of this paper.

Oil-producing microalgae are an extremely attractive alternative to conventional fuel sources as they grow extremely rapidly, have the potential to produce as much as 100 times more oil per hectare of land area than land-based crops, and if properly developed, can serve as a biofuel source that is economical, sustainable, reduces global warming, reduces the need to displace conventional food crops, and provides energy-independence (1,2,3). In addition, algae farming has the potential to generate 50 – 100 times more oil production than that of competitive soy or corn based crops thereby significantly increasing monetary crop yield per acre to the algae farmer.

Algae is typically grown in large ponds, raceways or tubes, to a concentration of 0.3 g/L or higher. After growth, the algae must be harvested, thickened and dried prior to lipid extraction. The water that is separated from the algae is returned to the growth medium, minimizing costly water loss and preventing expensive transport of water to the refinery. Perhaps one of the largest technical/cost hurdles to commercialization of biofuels is efficient cultivation methods including dewatering/drying of the algae prior to final oil extraction processes. There are a number of technologies available (Table I), the application of which depends upon the starting and desired finishing algae concentration, rate and thoroughness of algae recovery, and cost (Figure 1).

Currently, algae concentration is focused on the application of centrifugation, possibly using additives to flocculate the algae. Centrifugation is a highly energy intensive process and the flocculants often times introduce impurities that can foul the fuel without further post processing, resulting in either choice being less attractive and with a reduced net energy yield of the oil.

TABLE I. Advantages/Disadvantages of Various Dewatering Technologies.⁴

Technology	Advantages	Disadvantages	Capital/ Operating Cost
Centrifugation	High throughput, high recovery	High energy use (93%), batch process, shear forces	\$125k / \$0.53/m ³
Filtration	High recovery, dependent on particulate size	High energy use (89%), filter clogging or insufficient capture	
Chemical Flocculation	Increases algae size/clumping	Biomass contamination , high salt dosages	
Air Flotation	Captures small algae	Low removal efficiency	\$119k / \$0.47-0.55/m ³
Gravity Sedimentation	Low energy requirement, low-\$\$ products	Highly dependent on algae density and size (larger is better)	\$33k / \$0.14-0.22/m ³

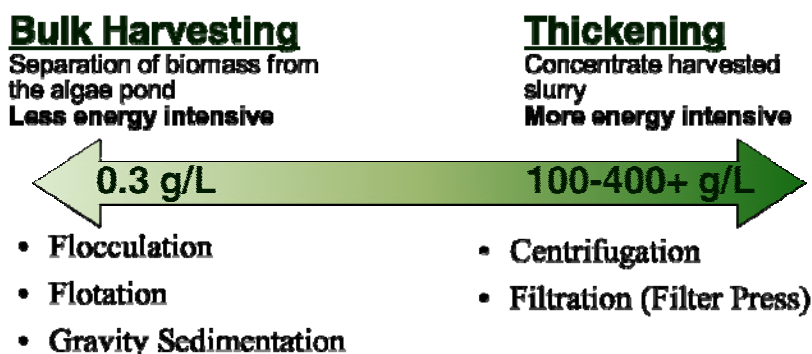


Figure 1: Selection of dewatering technology depends upon cost-competitive price point, as it pertains to starting and ending algae concentration.

Technical Approach

FARADAYICSM ElectroConcentration provides an alternative dewatering technology. The major advantages of the FARADAYICSM ElectroConcentration Process as compared to centrifugation (with or without chemical flocculation) are: 1) relatively low energy application, 2) no required chemical additives, 3) no required post processing, and 4) lower overall cost. FARADAYICSM ElectroConcentration is based on the principles of electrophoretic processes that involve the migration of small, suspended particles in a liquid driven by a constant electrical potential difference. The process has found applications ranging from nanoparticle composites to large colloidal molecules, including deposition of paint primers to steel, phosphors in the manufacturing of screens for advanced information displays,^{5,6,7} solid oxide fuel cell components

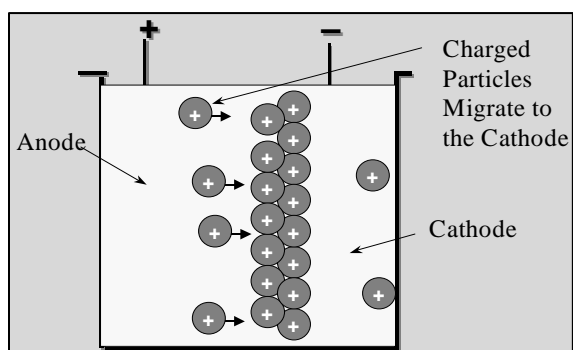


Figure 2: Principles of electrophoretic processes.

and functionally graded materials. Electrophoresis has the benefits of high particle movement rates, non-line-of-sight movement, simple processing equipment, low levels of contamination, and reduction of waste relative to many wet solution type processes. Figure 2 shows the basic principles of the electrophoretic process. Two electrodes are suspended in a processing bath. For positively charged particles, the cathode is the target and the anode is the counter-electrode. The process bath consists of a stable suspension of the material to be moved. When the voltage is applied, the charged particles in the suspension migrate towards the cathode under the influence of the electric field and can coagulate into a dense mass. It is also possible for particles to be negatively charged and to move towards the anode. Under constant voltage control, the drift velocity of spherical particles in suspension can be expressed as Equation (1):^{8,9}

$$V = \frac{2}{3} \varepsilon_0 \varepsilon_r \zeta \eta^{-1} (df/dx) \quad (1)$$

where ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the solvent, ζ is the zeta potential of the particle, η is the viscosity of the solvent and df/dx represents the strength of the applied electric field. The drift velocity is likely to affect the processing rate as higher drift velocities will yield greater algae movement, and therefore faster concentration. Equation (1) suggests that the drift velocity of the spherical particles (in this case, algae) in the suspension is a function of the applied electric field. This implies that the homogeneity of the electric field (i.e., the “current distribution”) is important for a uniform, energy efficient electroconcentration process through controlling the distribution of the concentrated algae mass.

FARADAYICSM ElectroConcentration applies pulse/pulse reverse electric fields to the electrophoretic process, enhancing the process capability and enabling: 1) reduction of hydrolysis, 2) improved pH stability, 3) improved electric field control, 4) control of the concentrated mass thickness/volume, 5) improved movement in recessed or hidden areas, and 6) a higher energy efficiency due to targeted processing. A pulse/pulse reverse waveform (Figure 3) is an interrupted, asymmetric pulsed waveform characterized by a cathodic period followed by an anodic period and an off time. The waveform parameters are: (1) the anodic pulse current density, i_a , (2) the anodic on time, t_a , (3) the cathodic pulse current density, i_c , (4) the cathodic on time, t_c , and (5) the off-time, t_o . The sum of the anodic and cathodic on times and the off time is the period, T , of the modulation. The inverse of the period is the frequency, f , of the modulation. The anodic, γ_a , and cathodic, γ_c , duty cycles are the ratios of the respective on times to the modulation period. The average current density (i_{aver}) or net deposition rate is given by:

$$i_{aver} = i_c \gamma_c - i_a \gamma_a \quad (2)$$

Just as there are infinite combinations of height, width, and length to obtain a given volume, in pulse/pulse reverse process there are unlimited combinations of peak current densities, duty cycles, and frequencies to obtain a given deposition rate. These parameters provide the potential for much greater process/product control compared to DC processing. With improvements in the output, control and accuracy of available pulse/pulse reverse power supplies, pulse/pulse reverse electroplating has come into its own.¹⁰ These same principles bring similar advantages in electrophoretic processes.

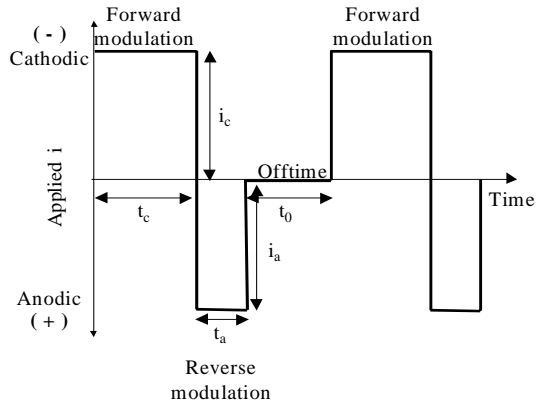


Figure 3: A FARADAYICSM waveform.

Preliminary Results

S. dimorphus was the algae species of choice to this program. This algae species grows in fresh water, has flagella, and can carry up to 1/3 of its mass as oil. Initial ElectroConcentration feasibility studies were performed in a 500 ml beaker. Electrodes were suspended vertically in the beaker, which was filled with the algae containing pond, and a DC electric field was applied between the electrodes. Figure 4 shows a typical test result, visually comparing the distribution of algae in solution before and after the 20 minute test. At the completion of the Electroconcentration process, there was a dense, floated mass of algae at the top of the beaker, a low concentration region around the electrodes, and an unconcentrated region below the electrodes at the bottom of the beaker. A further comparison of these regions is given in Figure 5; cell counts indicated that the algae solution at the bottom of the beaker did not differ in concentration from the original pond, the electrode region had been depleted by ~8 times and the top had been concentrated by ~12 times.

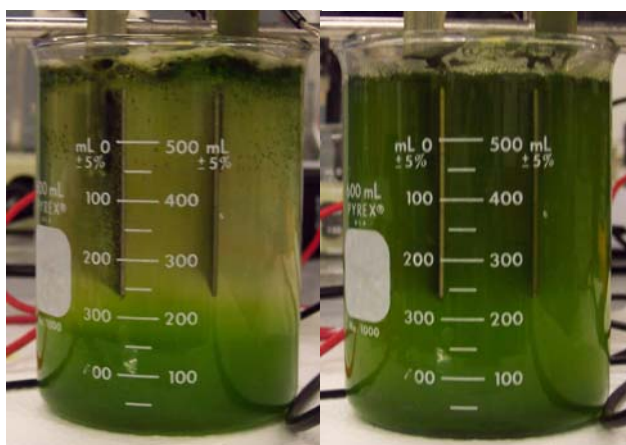


Figure 4. Comparison of the separation of algae using the FARADAYICSM ElectroConcentration Process (left) and gravity assisted settling (right).

Left: Algae depleted water (8x or more depleted)
Middle: “Pond”-level concentration
Right: Concentrated algae (12x or more concentrated)



Figure 5. Demonstration of the ability to purify pond water (left), initial solution (middle) and concentrated algae (right) using the FARADAYICSM ElectroConcentration Process.

Figure 6 compares DC and FARADAYICSM processing, using a cell that more effectively focused the electric field to just the area between the electrodes, to increase process efficiency. A 50 V DC waveform was applied for 10 minutes, resulting in a depletion of ~180 times. While this result is impressive, the depletion is likely far in excess of that required. Furthermore, the energy required to achieve this level of dilution (204 W.hr/L) is extremely high and would lead to unwanted cost. The purity of concentration achieved in this test may be of interest to applications where high levels of separation of the algae from the source solution are required, for example, nutraceuticals and drug recovery.

By comparison a FARADAYICSM waveform consisting of a 20% on time at 50 V, 80% off time (0 V), at a frequency of 100 Hz was applied to the cell for 4 minutes. The foamy mass on top of the cell was ~32 times more concentrated than the starting suspension. In comparison to the DC process (Table II), this test (8 W.hr/L) used ~25 times less energy.

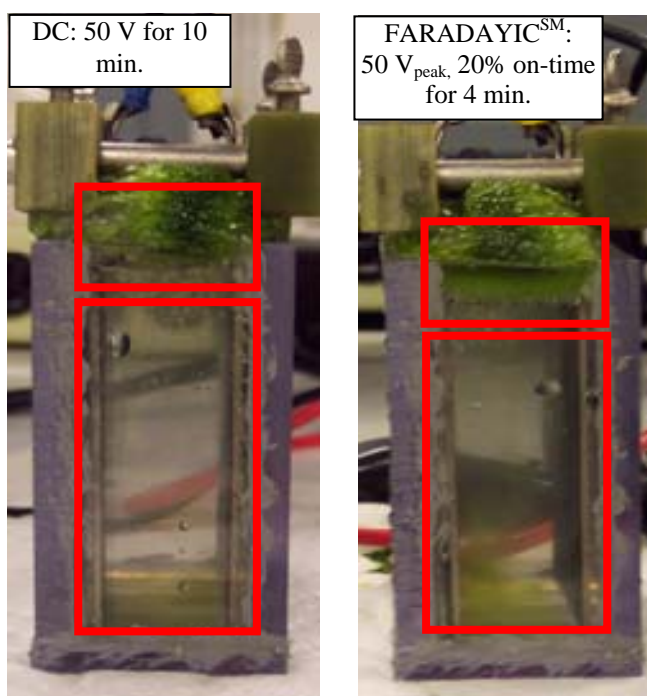


Figure 6: Comparison of DC and FARADAYICSM processing at the completion of the ElectroConcentration Process. Red boxes indicate concentrated floating mass (top) and depleted electrode zone (bottom).

Table II also gives data for the volume of H₂O electrolyzed during the ElectroConcentration process. The data shows that even if all of the applied energy were utilized to directly electrolyze water in the bath, only a relatively small volume of water would be electrolyzed. This is important, as it is desirable to limit the amount of water removed (electrolyzed) so as to return the maximum amount of water back to the pond. As even small amounts of water loss may accumulate over time, it is worth noting that the PC test electrolyzed a much smaller amount of water (0.04 $\mu\text{L}/\text{L}_{\text{solution}}\cdot\text{min}$) than the DC test (4.6 $\mu\text{L}/\text{L}_{\text{solution}}\cdot\text{min}$).

Table II: Comparison of DC and FARADAYICSM processing at the completion of the ElectroConcentration Process.

Electric Field	DC @ 50 V	FARADAYIC: 50 V _{peak} , 20% on, 100 Hz
Time	10 min	4 min
Current	1.3 – 3.0 A	1.2 – 1.4 A
Concentration in Flotation Region	Foam overflowed cell	32x
Depletion in Electrode Region	180x	13x
Observations	Vigorous electrolysis, boiling	Minor electrolysis
Energy per vol.	204 W.hr/L	8 W.hr/L
H ₂ O Electrolyzed	4.6 μL/L _{solution} .min	0.04 μL/L _{solution} .min

Scaling Up the Process

While the initial results are promising, additional work needs to be done to better elucidate the mechanism by which separation occurs, and to scale-up the process. 5 x 5 x 5 in benchtop cells have been constructed to investigate the effect of electrode orientation (horizontal - small or large gap, vertical), waveform parameters, nucleation time, integrity of the algal cell structure post-processing, and the energy/cost required per volume to go from 0.3 g/L to X g/L on Harvesting-Thickening continuum. Once cell and process parameters have been optimized, the focus will shift to scaling up the process.

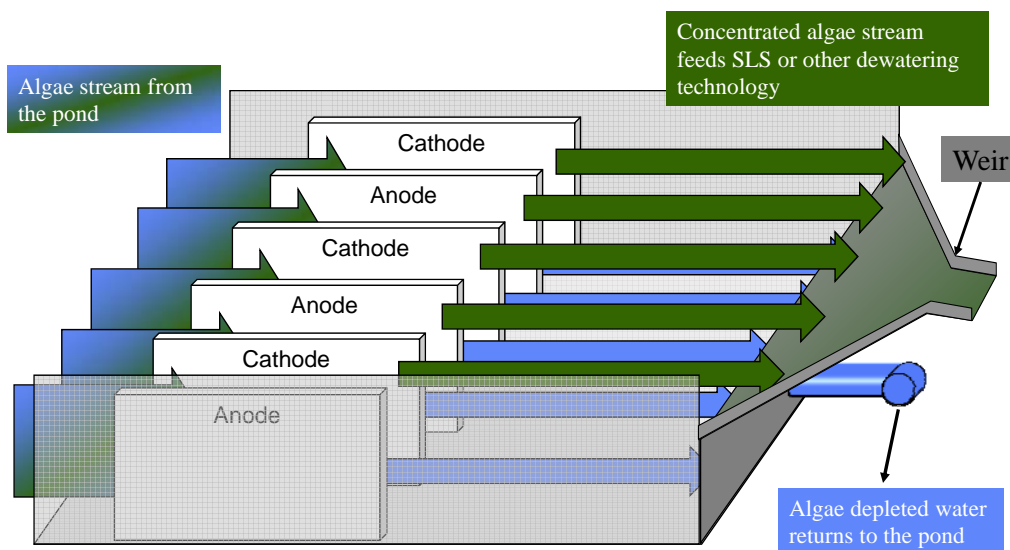


Figure 7: FARADAYIC[®] ECP flow channel system using multiple vertical electrodes for the preconcentration of algae.

Figure 7 shows a schematic for the FARADAYIC[®] ElectroConcentration flow channel system. In this concept, water with a dilute concentration of algae (i.e. from the pond) is introduced into the flow channel at the left. The dilute algae suspension then enters into the

processed region, where the electrodes are located, and the algae are separated from the water. Although the electrodes are presented in the schematic as multiple, vertical electrodes, they can have other configurations, such as a pair of vertical electrodes or a pair or multitude of horizontal electrodes, to be determined by optimization experiments to be the most advantageous. The floated and concentrated algae then travels to a weir, which will collect the algae for thickening/drying. The algae-depleted water, which still has a small amount of algae in it, ~ 5% of the original concentration, can then be returned to the pond as a new culture, or disposed of, as required by the end user.

Figure 8 shows the prototype flow channel, which is 5 in (w) x 5 in (h) x 12 ft (l). The algae suspension will be pumped from drums into and out of the cell ends by peristaltic pumps. The inlets will be designed to induce as little turbulence as possible into the cell, with final designs expected to be similar to that seen in Figure 7. Thermocouples are located every 2 feet to monitor temperature. The anticipated control variables include electrode spacing and orientation, and flow rate. The design for the flow channel was based on the desire to process large volumes of algae over a range of flow rates. High flow rates may not be advantageous due to the difficulty in maintaining lamellar flow, which could minimize mixing of the concentrated algae and the depleted water during processing.



Figure 8: 12 ft x 5 in x 5 in flow channel constructed at Faraday for continuous processing of bioalgae pond solution.

Conclusions

The FARADAYICSM ElectroConcentration process has been demonstrated to concentrate algae in a process stream for preconcentration/dewatering for biofuel production. Initial experiments concentrated the algae biomass up to 32x, while depleting the pond of algae by up to 13x. The process showed similar concentration capabilities to DC processing, but for significantly less energy and with much lower water loss due to electrolysis. FARADAYICSM ElectroConcentration doesn't contaminate the biomass during processing, as with chemical flocculation. It is anticipated that the FARADAYICSM ElectroConcentration process will compare favorably with alternative harvesting technologies although the economics have yet to be finalized.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. IIP-1058465. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF. Faraday gratefully acknowledges the Edison Materials Technology Center (EMTEC) and AlgaeVenture Systems for their support and assistance throughout this project.

References

-
- 1 Y. Chisti, *Trends Biotech.* **26**, 126-131 (2008).
 - 2 X. Meng, J. Yand, X. Xu, L. Zhang, Q. Nie, and M. Xian, *Renewable Energy*, **34** 1-5 (2009).
 - 3 G. W. Huber, S. Iborra, and A. Corman, *Chem. Rev.* **108**, 4044-4098 (2006).
 - 4 Mohn, F.H., *Harvesting of micro-algal biomass, Micro-Algal Biotechnology*, Cambridge University Press, p 395-414, 1988
 - 5 M.J. Shane, J.B. Talbot, R.D. Schreiber, C.L. Ross, E. Sluzky, and K.R. Hess, *J. Colloids and Interface Sci.*, **165**, 325 (1994).
 - 6 J.B. Talbot, E. Sluzky, and S.K. Kurinec, *Journal of Materials Science*, 39(3): 771 (Feb 2004).
 - 7 B.E. Russ, J. B. Talbot, and E. Sluzky, *J. Soc. Information Displays*, Vol.4, No.3, 207 (1996).
 - 8 Y. Hirata, A. Nishimoto, and Y. Ishihara, "Forming of Alumina Powder by Electrophoretic Deposition", *Seramikusu Kyukai Ronbunshi*, **99**, 108 (1991).
 - 9 H. Tamura Y. Matsuda, *Gendai Denki Kagaku*, 92 (1987).
 - 10 E.J. Taylor, *et al.*, Electrically Mediated Plating of Semiconductor Substrates, Chip Scale Packages and High Density Interconnect PWBs, *Plating and Surf. Fin.*, **89**, 88 (May 2002).