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SEPARATION METHODS IN THE ALGAE TECHNOLOGY

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Carbon dioxide is the air pollutant emitted in the greatest volume nowadays. Capturing and deposition of carbon dioxide require great financial effort. Spontaneous processes exist in nature that can be the basis of re-introducing CO_2 into the biological system. A number of valuable products can be obtained including motor propellants. Nowadays petrol companies all over the world invest increasingly more funds into algae technology research, and there are researches going on in the energy, cosmetics, pharmaceutical, and food industry for marketable microalgae components. The viability of the technology is determined by its energy-needs which are mainly affected by the separation of the biomass from the reproduction medium. In this paper, we look into the circumstances as well as the effects of flocculation-densification and ultrafiltration on the algae suspension.

Keywords: algae, lipides, separation, ultrafiltration, flocculation

Introduction

Microalgae used for energy production take up compounds they need to build up their organizations from aqueous solutions. On one hand they need inorganic salts and simple organic compounds from the nutrient solution, on the other hand they need CO_2 (exhaust gas) that is introduced to the reaction vessel [1].

Light available for the culture (a mass of photosynthesizing organisms) is basically a limiting factor, a reason for which special photobioreactors had to be used for guaranteeing the optimal reproduction conditions [2–5]. Some of the requirements for these reactors are that they have to let the specific spectrum of sunlight needed for photosynthesis pass, and they have to be weather-resistant.

Flat-type closed photobioreactor panels are operated in semi-batch mode at the Department of Chemical Engineering of the University of Pannonia. The reactors were specifically planned using special construction units in order to maximize the productivity of the biomass in the local microclimate *(Figure 1)*.

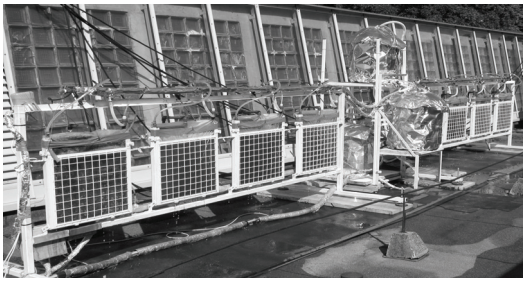

Figure 1: Algae cellfactory: large-scale laboratory photobioreactor installed outside with natural lighting

Removal of the algae suspension from the propagation system

Harvest is the line in time separating the biologically active and inactive phases. In order to make a proper choice, the behavior of the specific algae species and the added nutrient solution and environmental parameters have to be known. Propagation phases are well-resolved life-cycles of the alga population in the reproduction curve.

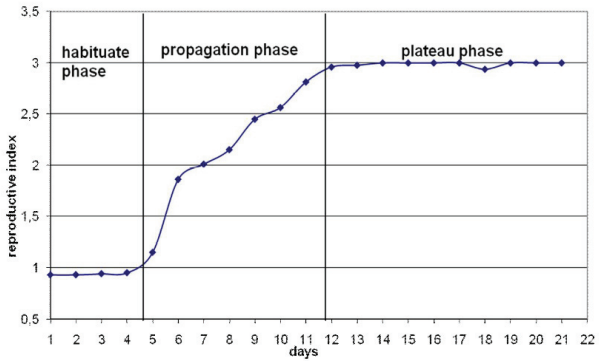

Figure 2: Reproduction phases of microalgae; reproduction curve

In certain cases, a fourth cycle can be observed after the plateau phase showing a decreasing tendency. In this cycle, cell death occurs because of viruses or bacteria or because some other vital parameter is affected.

According to our experience, such a population becomes inviable; the change can only be reversed at the cost of large amounts of energy. The suspension has to be processed as soon as possible and restarted with a fresh inoculation culture.

Harvest can be done by microfiltration, centrifugation, flocculation [6], sonochemical processes, or with other techniques currently under development [7]. Membrane separation methods were given special attention along with chemical flocculation, clarification, and autoflocculation.

Experimental

Flocculation

Microfiltration was carried out after the settling experiments with G4 glass filters under vacuum (created by a water aspirator).

The needed current quantity of the flocculant and the additives can be determined by measuring the parameters of the algae suspension (pH, particle charge, concentration/ floating mass percentage). Because of this, only the interval of the added quantities can be given at the description of the experiments.

Purification

Addition of NaOH to the mixture is advantageous in the later phases of processing (cell wall destruction). NaOH also decreases the specific charge density [8–10]. Hence, the first experiments consisted of increasing the pH to 10.5. During the experiments, the freshly harvested and still reproducing algae mixtures exhibited excellent flocculation and appropriate (average) speed of sedimentation (6×10^{-3} m/s). For algae mixtures in the plateau phase (that do not reproduce any more) this method proved ineffective, making a further additive necessary to increase the sedimentation speed.

When setting the pH with NaOH, an additive was given to the mixtures in order to help the coagulation and settlement of floccules. Iron(III)sulfate (3–6 cm^3, depending on the concentration and pH of the suspension; $c(Fe_2(SO_4)_3) = 150$ g/dm^3 per 1 g of algae mixture) evidently helps the processes of flocculation and sedimentation (1.4×10^{-2} m/s). After sedimentation, a solid alga layer remains at the bottom of the mixture. In spite of the excellent sedimentation, further experimentation was needed since the added iron makes it difficult to perform subsequent analysis and processing.

Iron(III)sulfate was replaced with a cationic flocculant that we also used for the analytical measurements, namely poly(diallyldimethylammonium chloride) (polyDADMAC; 60–100 cm^3 depending on the PCD values; c (polyDADMAC) = 2.4 g/dm^3 per 1 dm^3 of algae mixture). This sedimentation method proved effective in most of the experiments, but the speed of sedimentation is significantly lower (7.6×10^{-3} m/s), which needs improvement.

The sedimentation measured in the former experiment can be accelerated by adding less flocculant to the alkalified solution (approximately 35% less in comparison to the previous experiments; 39–65 cm^3 polyDADMAC / 1 dm^3 algae mixture) and significantly less iron(III)sulfate (approx. 60%; 1.2–2.4 cm^3 $Fe_2(SO_4)_3$ / 1 dm^3 algae mixture). The results show excellent flocculation and appropriate speed of sedimentation (2.2×10^{-2} m/s).

After setting the pH to 10.5, sedimentation of the algae mixtures can appropriately be carried out in the concentration intervals given in *Table 1*.

Table 1: Optimal concentration intervals relative to the cationic flocculant and Fe^{3+} ions

Lower concentration interval (g/dm^3)	Additives	Upper concentration interval (g/dm^3)
9×10^{-2}	P-DADMAC	1.5×10^{-1}
5.2×10^{-1}	Fe^{3+}	1

A comparison of the experiments is given in the diagram of *Figure 3*.

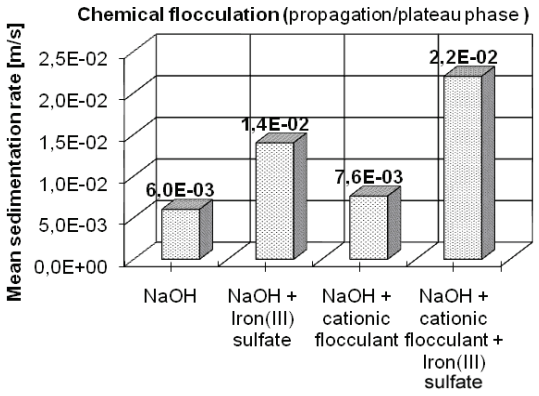

Figure 3: Results of the chemical flocculation experiments

Ultrafiltration

There are problems associated with the above-mentioned densification processes, namely that (1) they need the addition of chemicals and (2) that problems can arise associated with upscaling (e.g. the continuous dispersion and mixing of the flocculant in the suspension, etc.). For these reasons, membrane separation and ultrafiltering were also added to the examined processes aiming to improve usability.

The ultrafiltration membrane divides the original mass current (algae suspension) into two parts.

One of them passes the membrane (this is the permeate: filtered nutrient medium), while the other is the concentrate (in our case, the densified alga suspension).

For the densification and purification experiments, a PLC controlled device at the Department of Chemical Engineering of the University of Pannonia was used that is equipped with a ZW-10 module.

According to the direction of the permeate flow, the device is conducting an outside-in process. The measurements were carried out with a Zenon ZW-10 immersion module. According to the specification, the

membrane is capable of retaining particles under 1 µm, hence capable of the concentration of our micro algae cells [11–13].

The module works as a sub-unit of a PLC controlled device.

During the operation of the device, the microalgae suspension is introduced in the technical vessel. This is a rectangular cuboid with a volume of 30 dm^3. The vessel is equipped with a level sensor, a pH probe and a thermometer.

The permeate (filtered nutrient medium) is introduced into a permeate vessel of 10 dm^3, from which the permeate requirement of the backwash is provided. Periodic removal of the permeate can be carried out at the sampling outlet, whereas continuous removal can be carried out through the overflow pipe.

Densification with membranes

The suspension in the densification vessel was pneumatically mixed by a vaporizer propelled by an air compressor. After this, sample refill was carried out with a 1 dm^3 graduated cylinder in order to minimize fluctuation of the liquid level. To gain the maximal data possible from the processing of the available samples, the measurement was divided into a number of sections. The algae suspension for the filtration experiments was sampled in 40 dm^3 portions from the photobioreactor.

After densification of the 40 dm^3 volume to 20 dm^3, the suspension was washed with distilled water. The washing was continued until the complete removal of remaining salts and other organic material and metabolites.

The extent of cleansing of the permeate was checked by measuring the dry matter content and electrical conduction. The total dry matter content of the suspension was measured (along with remaining salts). This experiment was used for both the analysis of the concentrate and the permeate.

The following 40 dm^3 of algae suspension was densified according to the procedure given above and coded *UF2*. These experiments were conducted 7 times (*UF1*-*UF7*).

For the complex examination of the filtration, the washed concentrate from the previous densification (concentrated algae suspension) was added to the current concentrate. Washing makes it possible to exclusively analyze and process the dry matter content of the suspension of microalgae cells in distilled water. Further advantageous properties were shown in comparison to the retentate, as e. g. ease of storage (later onset of decay) and faster evaporation.

The densification experiments were conducted until reaching the maximum algae production capacity. The cleansing (washing with distilled water) was carried out until the lowest possible conductivity values.

The trends of change in dry matter content and the related conductivity of the permeate were identical in most of the cases.

Figure 4 shows the relationships between the total dry matter content relative to the algae content of the initial suspension and the permeate conductivity. The data were gathered at the initiation of filtering both from the initial suspension and the permeate outlet. The figure shows the definite tendency and connection between the quantities measured at both sides of the membrane. According to the measurements so far, there is an unambiguous connection between algae contents of the total dry content of the algae suspension and the conductivity of the permeate. The higher the algae concentration is, the higher the initial conductivity is.

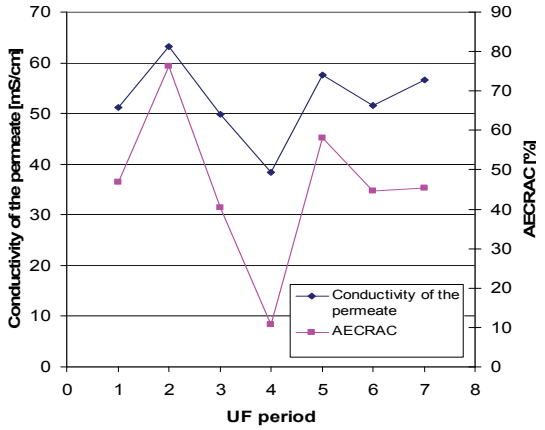

Figure 4: Conductivity of the permeate vs. all extract content of the initial suspension referred alga cell content (AECRAC)

Similar values were obtained for the permeate flux by all measurements. This means that the device is capable of filtering suspensions of different compositions and concentrations in the examined interval.

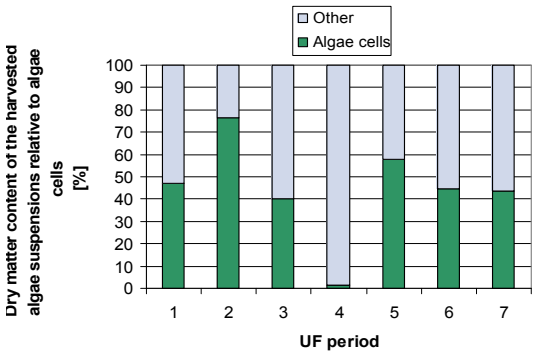

Figure 5: The dry matter content of the harvested algae suspensions relative to algae cells

An algae suspension from a photobioreactor unit operated in natural circumstances was processed in the second *UF* period of *Figure 5*. Further correspondences can be brought to light by examining samples from different reactor units at different reproduction stages. Additional analysis would allow far-reaching conclusions in regard of cultivation and implementing these conclusions into the technology further increasing the biomass capacity.

The initial algae suspension (40 dm^3) was densified from 13 g/L (algae cells, metabolites and salts) to 6.1 g/L (20 dm^3; only algae cells). The final algae concentrate has a concentration of 30.4 g/L of microalgae in a volume of 20 dm^3.

Results

We have defined the components of a flocculant mixture for optimal use (NaOH + polyDADMAC + $Fe_2(SO_4)_3$, minimized the chemicals needed for the mixture (NaOH until pH = 10.5, 39–76 cm^3 polyDADMAC, 1.2–2.4 cm^3 $Fe_2(SO_4)_3$ / 1 dm^3 algae mixture). With the flocculant, the concentrate can be gained quicker and by using less energy, but the remainders of the chemicals pose problems in further processing.

Summary

With the evaluation of the results of our ultrafiltration experiments it can be concluded that, according to the values of the permeate flux, our device is capable of filtering suspensions of different compositions and concentrations in the examined interval.

After ultrafiltration, it is possible to remove the accompanying compounds, which makes the concentrate more stable and manageable. This is advantageous from a research and development point of view because later processing and analysis are not affected or are only affected to a definable extent. If it is an aim to recycle the nutrient medium (re-use of the remaining salts), the highest priority must be given to the membrane separation methods.

Considering the membrane separation results and the permeate analysis, the presence of a number of metabolites can be assumed in different concentrations. These can all be separated from the valuable microalgae cells.

Acknowledgements

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