PROBLEMS OCCURRING DURING THE PROCESSING OF MICROALGAE PROPAGATED FOR OIL PRODUCTION

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ABSTRACT. At the University of Pannonia we study algae cultures used to clean industrial wastewater and to absorb industrial carbon dioxide. Amongst others, in the focus of our work are processing and separating operations. We aim to separate the algae from the nutrient solution the simplest and most economic way. Furthermore, we try to define the useful components of algae and their optimal extraction, based on the optimization of techniques of extraction and other economic and environmental aspects.

Keywords: *carbon dioxide absorption, microalgae, separation, flocculation, filtration*

INTRODUCTION

Microalgae are regarded as one of Earth's most efficient organisms because of their productivity and generally high oil contents. As for their productivity, microalgae are capable of doubling their biomass in 24 hours [1, 2, 3, 4]. According to a literature survey, their oil content is 20 % on the average (certain algae species can reach 60-80 %) [1, 5, 6, 7]. Research in oil production from algae is mainly focused on microalgae. These are photosynthesizing organism the size of which does not exceed 0.5 mm. They are, with a good chance, a solution to the reduction of carbon dioxide and nitrous oxides, because they transfer them in a photosynthetic pathway [8]. The product of this process contains a significant amount of solar energy stored in chemical bonds, and as a result, "high volumes" of biodiesel can be retrieved from them [4, 9, 10, 11]. In addition to the above mentioned, microalgae are not only capable of cleaning exhaust gases, but they also utilize certain components of wastewaters, this way cleaning them. The contamination provides additional nutrients for the algae, starting their exponential growth.

Whatever the advantages, the biggest obstacles are the expenditures. The harvest, dehydration, drying and the extraction of the lipids and their conversion are the most critical steps in the production of alga-based fuels

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because of their high investment and operation costs. The biggest challenge for the technology is cost-reduction, which can mainly be achieved at the separation steps.

The harvest can be carried out with microfiltration, centrifugation, flocculation [12], with sonochemical techniques, or with any other techniques [13] they are under development. Presently, the combined separation technology appears to be economically feasible. The combination of flocculation and microfiltration results in a separation of appropriate speed, quality and cost. The aim of this paper is to present the tendency of certain special alga species towards flocculation with the use of different techniques and flocculants. The flocculation of the algae can be achieved by two means. Firstly, with the so-called autoflocculation technique, secondly, by chemical means, e.g. by the addition of aluminum sulfide, iron chloride, or iron(III) sulfate [14] to the solution, which results in the coagulation of the algae [15, 16]. Of the two methods, chemical flocculation is capable of increasing the alga concentration more efficiently. Thus the experiments described in the followings deal with chemical flocculation too, examining the effect of different flocculants and their combinations with respect to the alga solutions.

RESULTS AND DISCUSSION

Autoflocculation experiments

The simplest way to achieve the phenomenon of autoflocculation is by the cessation of the carbon dioxide feed. When ceasing the carbon dioxide feed, the slow sedimentation of the algae commences. The roles and the effect on sedimentation of in-sprayed oxygen, irradiated light and temperature are not yet clear. The examination of the phenomenon is the subject of present laboratory measurements.

Cessation of the carbon dioxide feed

The experiment was carried out by taking samples of 500 cm^3 from the propagation reactor, from different alga species and at different states of propagation (Figure 1). The average rate of sedimentation was 3×10^{-9} m/s in the case of algae taken at the propagation phase, which is an unacceptably low value. The average sedimentation rate of the algae after the propagation phase was somewhat higher, 6×10^{-9} m/s, but this is still unacceptably low for us. Although the effect of the other parameters is still under investigation, this method does not seem feasible at present.

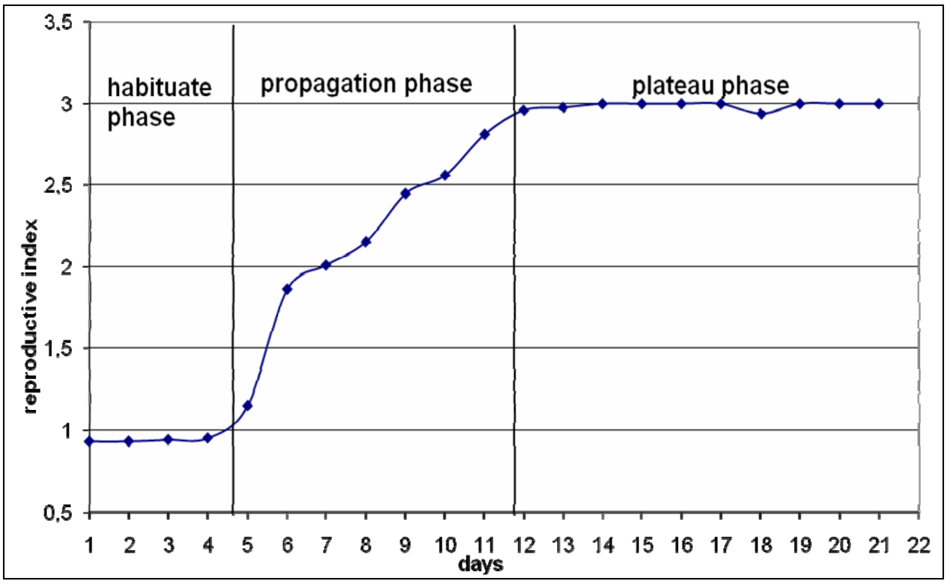

Figure 1. The reproduction of the microalgae

Flow choke with carbon dioxide

This is a novel approach to autoflocculation, which has been developed at the Institute of Chemical and Process Engineering of the University of Pannonia. The technology is an extension of the phenomenon of autoflocculation. The rates of sedimentation somewhat rise (Table 1), and a more complete sedimentation can be observed than in the former experiment (Figure 2).

Table 1. Comparison of autoflocculation experiments

	Autoflocculation method used	
Sedimentation of algae in the propagation phase	**Cessation of the CO_2 feed**	**Flow choke with CO_2**
mean sedimentation rate [m/s]	*3×10^{-9}*	*7×10^{-9}*
Sedimentation of algae after the propagation phase	**Cessation of the CO_2 feed**	**Flow choke with CO_2**
mean sedimentation rate [m/s]	*6×10^{-9}*	*9×10^{-9}*

Figure 2. Top part: the result of the cessation of the carbon dioxide feed; Bottom part: the result of flow choke with carbon dioxide

The analytics of the chemical flocculation experiments

The use of the Particle Charge Detector (PCD)

The colloidically solved particles and algae in the aqueous solution carry electric charge if they have dissociative functional groups on their surfaces. If the counter-ions are separated from the particles, a flow potential can be measured (mV). In order to determine the quantity of charge polyelectric titration was carried out, in which the flow potential = 0 mV was used to indicate the end-point. To the sample was added a polyelectrolite of opposing charge (poly-diallyl-dimethyl-ammonium-chloride; Poly-DADMAC) as a titrating agent the charge quantity of which is known. The effect of the flocculants was followed by PCD measurements and defined with the clarification experiments. It is important to note that the potential is hard to reproduce because it is also dependent on different external factors (temperature, molar weight, particle size, etc.). These also make the interpretation of the results difficult. (Because of the great amount of experimental datas and the complex correlation between them, correlation analysis needed to achieve better understanding.)

Experiences gained with the measurements: 1. the shape of the titration curve is dependent on the alga species, 2. the specific quantity of charge is a function of the propagation phase, 3. the specific quantity of charge decreases with the increase of pH, 4. the specific quantity of charge somewhat decreases over time.

Clarification experiments

Sedimentation with basification

The addition of NaOH to the mixture is advantageous in the later steps because it decreases the specific quantity of charge. Thus the first experiments meant increasing the pH to 10-11. As for the freshly harvested algae that were still in the propagation phase, excellent flocculation and appropriate rate of sedimentation (6×10^{-3} m/s) was observed. In the case of plateau phase algae mixture the procedure was uneffective, so to increase the rate of sedimentation, we needed an additional additive which accelerates the sedimentation of the flakes.

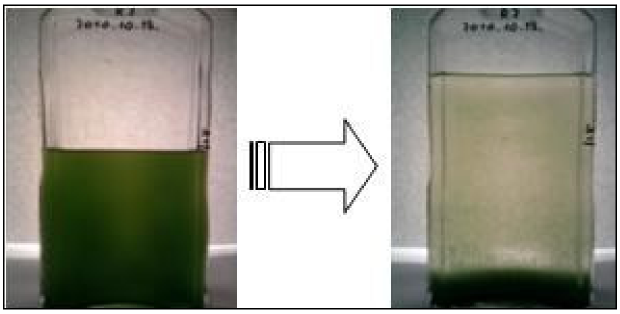

Figure 3. Sedimentation achieved with NaOH (freshly harvested algae, from propagation phase)

Sedimentation with basification and the addition of additives

Iron(III) sulfate was added (3 – 6 cm^3 $Fe_2(SO_4)_3$ / 1 l algae solution) to the basified solution and it was found that this enhances the process of flocculation; and after quick sedimentation ($1,4 \times 10^{-2}$ m/s) a thick layer of algae remained on the bottom of the mixture. Although the sedimentation is excellent, further experiments should be carried out because the additional iron makes the subsequent analytics and signal processing difficult.

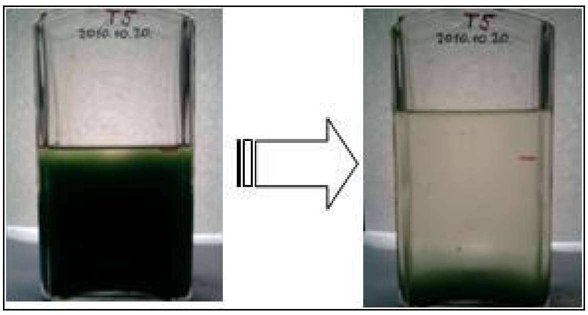

Figure 4. Sedimentation achieved with NaOH + $Fe_2(SO_4)_3$

Addition of NaOH and cationic flocculant

The $Fe_2(SO_4)_3$ was replaced with a cationic flocculant, polyDADMAC, which was used for the analytical measurements ($C_{P\text{-}DADMAC}$=2,4 g/l: 60 – 100 cm^3 Poly-DADMAC / 1 l algae solution). In the near future we plan to utilize cationic starch derivatives both for cost efficiency and for environmental protection reasons. The results were acceptable in most of the experiments, but the rate of sedimentation is significantly lower (7,6 × 10^{-3} m/s) than in the former experiment. An increase in the rate is necessary.

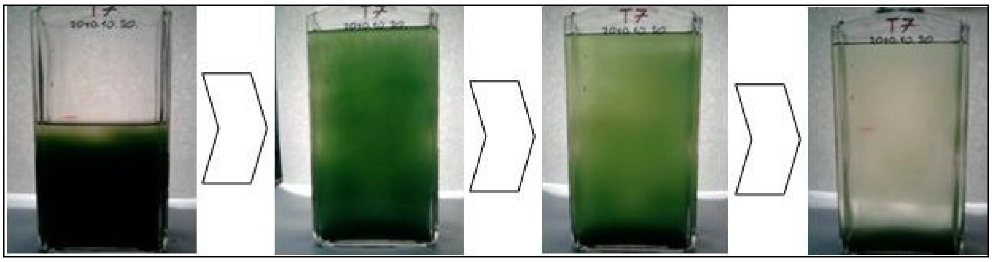

Figure 5. Sedimentation achieved with NaOH + cationic flocculant

Addition of NaOH, cationic flocculant and $Fe_2(SO_4)_3$

The former experiment can be accelerated by adding less flocculant and substantially less $Fe_2(SO_4)_3$ to the basified solution then earlier. (39 – 65 cm^3 Poly-DADMAC/ 1 l algae solution and 1,2 – 2,4 cm^3 $Fe_2(SO_4)_3$ / 1 l algae solution) The result was spectacular with excellent flocculation and appropriate rate of sedimentation (2,2 × 10^{-2} m/s).

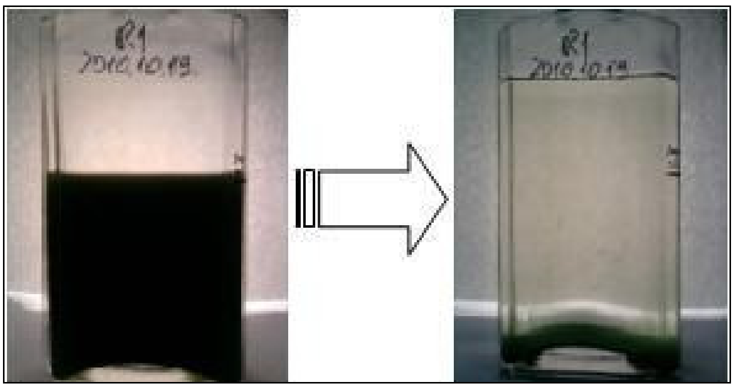

Figure 6. Sedimentation achieved with
NaOH + cationic flocculant + $Fe_2(SO_4)_3$

RESULTS

The autoflocculation experiments show satisfactory results, but because of the low settling speed we have not adapted the procedure in practice. The examined phenomenon – called CO_2 choke – we will study further, and want to develop a usable procedure in practice. The need of chemical substances have been optimized (the composition of the flocculation agent is the variable of the separation method). ((Use NaOH 10 -11 pH + 39 – 65 cm^3 Poly-DADMAC + 1,2 – 2,4 cm^3 $Fe_2(SO_4)_3$) / 1 l algae solution.) Table 2 shows the summarized and averarged results of our investigation.

Table 2. Results of the flocculation experiments

Life cycle	Time between harvest and preparation [h]	Sedimentate procedure	Mean sedimentation rate [m/s]
propagation phase	*independent*	Cessation of the carbon dioxide feed	$3*10^{-9}$
propagation phase	*independent*	CO_2 choke	$7*10^{-9}$
plateau phase	*independent*	Cessation of the carbon dioxide feed	$6*10^{-9}$
plateau phase	*independent*	CO_2 choke	$9*10^{-9}$
propagation phase	0-12	NaOH	$6*10^{-3}$
plateau phase	0-36	NaOH	0
propagation/plateau phase	0-36	NaOH + Iron(III) sulfate	$1,4*10^{-2}$
propagation/plateau phase	0-36	NaOH + cationic flocculant	$7,6*10^{-3}$
propagation/plateau phase	0-36	NaOH + cationic flocculant + Iron(III) sulfate	$2,2*10^{-2}$

Figure 7 show the comparison of the experiments.

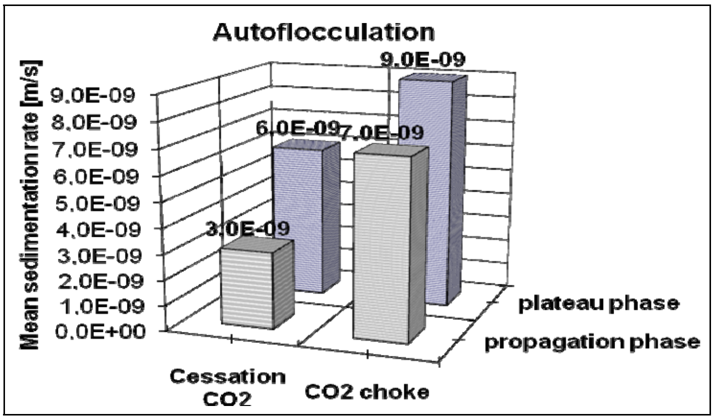

Figure 7/a. Results of the flocculation experiments

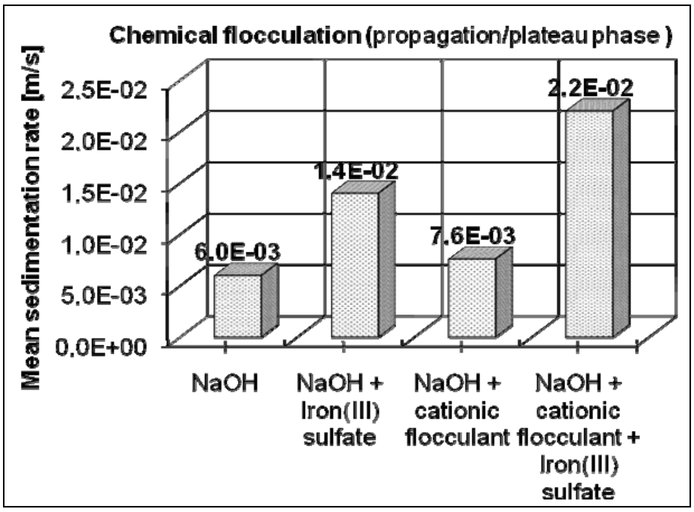

Figure 7/b. Results of the flocculation experiments

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