EFFLUENT TREATMENT BY MIXED ALGAE-BACTERIAL BIOMASS – PILOT EXPERIENCE

Janja Zule¹, Gabriele Weinberger², Corinna Hentschke², Ricardo Pereira³, Alp Erguensel³, Quentin Thiebaut⁴

IZVLEČEK

3AZISKAVE IN RAZVOJ

Raziskali smo možnost uporabe alg za čiščenje odpadnih vod v papirništvu. Gre za nadgradnjo konvencionalnega aerobnega čiščenja odpadne vode z uporabo mešane algno-bakterijske biomase. Specifične lastnosti mikroalg lahko v simbiozi z bakterijami pripomorejo k boljšemu ekonomskemu in ekološkemu efektu čiščenja. Zaradi izmenjave kisika in ogljikovega dioksida med avtotrofnimi algami in heterotrofnimi bakterijami ni potrebno zunanje prezračevanje, hkrati pa se izkorišča sposobnost alg, da vežejo toksične snovi, ki jih sicer bakterijski mikroorganizmi ne morejo razgraditi. Predstavljeni so rezultati pilotnega poskusa čiščenja papirniške odpadne vode z uporabo nove tehnike. Raziskave so potekale v okviru mednarodnega projekta "Albagua"

Ključne besede: čiščenje odpadne vode, algno-bakterijska biomasa, prezračevanje, flokulacija in posedanje, učinek razgradnje.

ABSTRACT

Possible application of algae for effluent treatment in the papermaking process was examined. The conventional aerobic waste water treatment process may be upgraded by utilization of a mixed algae-bacterial biomass. Improved economic and ecologic efficiency is expected on account of specific properties of microalgae and symbiotic action of both microorganisms. Due to interchange of oxygen and carbon dioxide between autotrophic algae and heterotrophic bacteria no external aeration is needed, while on the other hand the algae present are able to consume some toxic compounds which can not be digested by bacteria. The novel technology of effluent treatment and the results of a pilot test which was performed in real papermaking conditions are presented. The research was conducted within the international project "Albaqua" (http://www.cornet-albaqua.eu).

Key words: effluent treatment, algae-bacterial biomass, aeration, flocculation and settling properties, degradation performance..

1. INTRODUCTION

Paper mills are obliged to reduce emissions and improve their effluent quality due to strict EU environmental legislation. Many companies have already implemented biological treatment as secondary stage waste water purification process in order to improve overall efficiency and thus comply with environmental standards. Conventional aerobic treatment provides good results, however on the other hand it is quite energy demanding. For this reason innovative techniques intended to improve performance and reduce costs are constantly observed and examined. One of possible ways of how to make biological cleaning more effective is introduction of microalgae into the conventional stage using activated bacterial biomass (1-5). Heterotrophic bacterial organisms decompose organic impurities in water to CO₂ and H₂O for which they need oxygen which is conventionally supplied via aeration. An alternative source of oxygen supply may be autotrophic microalgae which consume available

CO₂ (provided by bacterial action) and H₂O during photosynthesis for which they use energy in the form of sunlight. Oxygen is released in the process as waste product. The latter can be conveniently used by bacteria for their heterotrophic degradation of organic impurities. Symbiotic co-existence of two types of microorganisms within the same effluent can be exploited for improved cleaning performance. Due to

efficient interchange of gaseous products between algae and bacteria no external aeration should be required, because all the necessary oxygen is to be provided by algae which at the same time efficiently consume CO₂ released by bacteria (figure 1). In addition, improved cleaning efficiency is expected due to specific ability of microalgae to consume toxins, heavy metals as well as nitrogen and phosphorous compounds.



Figure 1: Combined action of bacterial biomass and algae in effluent treatment plant

The main objective of our research was to introduce and optimize this innovative technique of biological effluent treatment first on laboratory level and than transfer the obtained experience and knowledge to pilot scale in real papermaking conditions in order to evaluate its potential and efficiency as alternative, energy saving effluent treatment technique.

The research was performed within EU sponsored Cornet "Albaqua" project (Combined algal and bacterial waste water treatment for high environmental quality effluents) which was coordinated by PTS (Papiertechnische Stiftung, Münich), and lasted 2 years. The other members of the project consortium were TUHH (Technische Universität Hamburg-Harburg), Celabor, Belgium, Pulp and Paper Institute, Slovenia and Paper Research Institute with Technical University, Hungary.

2. EXPERIMENTAL

In the first stage of the research it was necessary to examine which algae species were naturally present in papermaking waters, meaning that they were already adapted to technological conditions on the papermaking machines. Among 6 different species found, the microalga Chlorella Vulgaris proved to be suitable for further experiments, because of its specific properties, such as relatively quick growth and good flocculation with bacterial biomass. Subsequently algae were cultivated on laboratory level in order to produce the relevant quantity of biomass for further experiments. The experimental conditions for optimal growth, such as light intensity, mixing velocity, growth medium, pH and temperature, were carefully observed and optimized.

Effluent treatment tests with mixed algae-bacterial biomass were performed in small laboratory bioreactors after optimization of experimental parameters, such as hydraulic retention time (HRT), biomass concentration or dissolved and suspended matter (DSM), algae-bacteria proportion, fixation of biomass on carriers, nutrition load (C:N:P), sludge retention time (SRT), sedimentation time, O₂ concentration, temperature, pH and light intensity. Real effluents from several different paper production processes were used in laboratory experiments in order to determine purification performance.

Pilot tests were performed n the paper mill Goričane using waste water from different production programs. The paper mill produces different printing paper grades from primary fibers. So far it has

only chemo-mechanical waste water treatment plant which will have to be upgraded by a secondary stage water cleaning in order to improve effluent quality according to future legislation requirements. The schematic presentation of the pilot plant is shown in figure 2.



The pilot was equipped with two effluent collecting tanks (500 l), central bioreactor (500 I) equipped with mechanical stirrer and sensors for on-line measurement of temperature, pH, conductivity, redox potential and dissolved oxygen. The working volume of the bioreactor was 340 l. The pilot was operated for four months from July till November. In the beginning it functioned in batch mode for one month, while afterwards its operation was continuous. The volume of mixed algae-bacterial biomass was 116 l while the volume of effluent to be treated was 224 I. Effluent retention time (HRT) was 2 days in batch mode. A sedimenter unit (40 l) was added when the pilot worked in continuous mode in which case the active volume of the bioreactor was 300 l, the sedimenter volume 40 l, the daily effluent inflow and outflow was between 80 I and 90 I and the sludge return flow was 250 I daily. After some time the daily inflow/outflow volume of effluent increased to 195 l daily. During the pilot experiments some nutrients in the form of N and P salts as well as some fresh algae had to be added

Table 1: Pilot parameters

Parameter	Value
DSM (biomass concentration)	0,5–2,5 g/l
oxygen concentration	2–8 mg/l O2
temperature	15–30 °C
рН	7,5–9,5
light	natural daylight
HRT (hydraulic retention time)	1,8–3, 8 days
nutrients	N, P compounds
weather	sunny, cloudy, rainy

to the reaction mixture in order to keep it in optimal condition. Experimental pilot parameters are collected in table 1.

The efficiency of the pilot performance was determined by measuring the following effluent parameters before and

Figure 2: Effluent treatment pilot plant using mixed algae-bacterial biomass

after the treatment: COD, BOD₅, DOC (dissolved organic carbon), suspended solids, nitrogen and phosphorus compounds, such as NH₄, NO₂, NO₃, PO₄ as well as total phosphorus and nitrogen. ISO standard methods were used for the analyses.

Biomass concentration within the bioreactor was determined by DSM measurement. Algae content was characterized by spectrophotometric determination of chlorophyll concentration (6).

Biomass condition was also observed by microscopy in order that different microorganisms within the mixture were identified and their abundance evaluated. The condition of biomass in the reactor was monitored 5 times a week.

24 measurements of chemical parameters of input and output effluents were performed during pilot experiment. In batch operation incoming and outcoming water samples were collected at the start and in the end of each batch while the corresponding samples were collected twice a week during continuous work.

3. RESULTS AND DISCUSSION

It was established by laboratory experiments that algae could excellently integrate with activated sludge to form flocs. The latter showed good settling performance which was necessary for efficient separation of treated effluent from the remaining biomass. Fixation of mixed algae-bacterial mass on different plastic carriers was unsatisfactory. The microorganisms used did not need much time to adapt to experimental conditions including effluent characteristics. An exception were effluents from paper productions based on wood containing raw materials, most probably because of biocidal effects of some wood extractives. Other algae also appeared within flocs, meaning that a natural mix of microorganisms developed with time. In some cases Chlorella was the predominating species. Laboratory treatments of paper mill effluents with mixed biomass indicated good degradation results as the purification efficiency in most cases ranged between 70 % and 80 %. The calculations were based on COD removal. The best performance was observed when HRT was adjusted between 1 and 3 days, depending on the waste water COD, however for highly polluted waters (COD > 800 mg/l) this technology can not be suggested. The most suitable biomass concentration was between 1,5 g/l and 2,5 g/l and SRT value (sludge retention time) from 16 to 20 days. A sedimentation time of 2 to 3 hours could be easily achieved. Stirrers were needed in the system in order to keep the biomass suspended and ensure that all algae did come into contact with light.

No external aeration was needed. Oxygen concentration was sufficient during night as well. Additional aeration with blowers favoured heterotrophic bacteria so it had to be avoided. The colour of the biomass (intensive green) was a good sign of

system's health. 400 350 300 250 ng/l 200 150 100 50 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

Measurement

The laboratory results were confirmed by pilot experiment where overall treatment efficiency was similarly very high. COD and BOD values of inflow and outflow waters are presented in figures 3 and 4. The first 5 results were obtained in batch operation.

different production programs and consequently differently polluted waters. The removal of soluble organic material expressed as DOC was also very high as in most cases final effluent values after treatment approached 5 mg/l which was quantification limit.



Figure 4: BOD values of inflow and outflow effluents



Figure 5: Chlorophyll content of the reactor mixture

It is evident from the figure 3 that initial COD values differed significanly. The highest COD value of the incoming effluent was 337 mg/l and the lowest 70 mg/l. In most cases COD values of the output effluents did not exceed 30 mg/l which was the quantification limit. This meant that the efficiency of COD removal was very high despite

-input

- output

BOD values representing biodegradable organic compounds were also greatly reduced, in most cases the results did not exceed 3 mg/l which was guantification limit

Effluents from the paper mill did not contain much nitrogen and phosphorous compouds, such as nitrites, nitrates, ammonia and phosphates. The initial values for N-NH₄, N-NO₃ and N-NO₂ never exceeded 1,5 mg/l, however in most cases they were much lower. Inorganic phosphates P-PO₄ were never even detected.

The results of chlorophyll determination are expressed as mg per volume of reactor mixture and are presented in figure 5.

Chlorophyll concentrations moved between 2 mg/l and 12 mg/l which depended on various technological conditions. Concentrations were higher when there was enough N and P nutrients. The inflow waters were extremely poor in P and N compounds



Figure 6: Dry matter and ash content of the bioreactor mixture

so occasional addition of nutrients was necessary. Decrease of chlorophyll could have been partly ascribed also to the presence of different insects, such as larvae which abundantly used algae for food. Larvae had to be regularly physically removed.

Dry matter and ash content of the bioreactor mixture is presented in figure 6.

The values ranged between 0,9 g/l and 2,5 g/l with average value being 1,6 g/l. The lowest results were obtained when some degradation of biomass took place due to lack of nutrients. Inorganic portion of the dry reactor biomass averagely amounted to about 50 % of the total value. So only about half (44 – 63 %) of the reactor contents actually belonged to mixed algae-bacteria organic material. Most of inorganic matter was composed of carbonates, silicates, chlorides and sulphates (addition of Al2(SO4)3 in the first stage of water treatment) as well as the remaining nutrients.

A very important factor of the biomass condition and thus of the system performance was quantitative relation between algae and bacteria in the organic portion of the reactor mixture. The content of algae in the symbiotic mixture with bacteria moved between 40 % and 70 % which indicated that the system was most of the time in good equilibrium (most values around 60 % in favour of algae).

Microscopic examination of the reactor biomass showed that there were other microorganisms present, such as protozoa, flagellates, vorticella, euplotes and others, however Chlorella Vulgaris distinctively predominated.

4. CONCLUSIONS

Effluent treatment with mixed algaebacteria biomass worked well for the paper mill effluents without wood extractives at low and medium loads.

External aeration was not required as sufficient oxygenation was easily achieved by algae. Light intensity proved not to be a major factor as the pilot system worked also in dark and rainy days. Temperature and mixing had to be regularly monitored and optimized. Cooling (in summer) and heating (in autumn) within the bioreactor were conveniently achieved by available river water (18 °C) and effluent (37 °C). The system was in equilibrium when algae content was between 40 % and 60 % in the mixed organic biomass. The major threat for algae represented insects (Chironomidae larvae) that consumed algae, so physical barrier (net) had to be applied for protection. In additon, it was established by some preliminary experiments that the generated mixed sludge could be used as substrate for biogas production, especially if it was mixed with primary sludge in order to improve C/N ratio.

Further research will be needed to optimize this novel energy saving effluent treatment technology and transfer it to the industrial scale.

Acknowledgement

Authors would like to express gratitude to their national funding agencies for financial support.

Authors also greatly appreciate professional assistance of Borut Lazar and Robert Reinhardt from the company Algen Ljubljana by conducting pilot plant experiment.



LITERATURE

1. SAFONOVA, E., KVITKO, K., IANKEVITCH, M., SURKO, L., REISSER, W. Biotreatment of industrial wastewater by selected algal bacterial consortia. Engineering in Life Science, 2004, Band 4, Heft 4, str. 347–353.

2. PRECHTL, S., JUNG, R. Cost effective wastewater treatment with and algae reactor. Das Gas- und Wasserfach, 2002, Band 143, Heft 12, str. 872-877.

3. ASCHE, W. Utilisation of microalgae natural substances from underwater. Journal Seifen, Öle, Fette, Wachse, 1996, Band 122, Heft 1, str. 28-29

4. MEDINA-RODRIGUEZ, L. M. Floc formation in wastewater treatment systems using algal bacterial symbiosis. Hamburger Berichte zur Siedlungswasserwirtschaft, 2006, Band 59, str 1_110

5. NEIS, U., GUTZEIT, G. Biologische Abwasserreinigung mit symbiotischer Algen-Bakterien-Biomasse. Hamburger Berichte zur Siedlungswasserwirtschaft, 2002, Band 40, str. 159–168.

6. BARNES, B. A reappraisal of the use of DMSO for the extraction and determination of chlorophylls a and b in lichens and higher plants, Environmental and Experimental Botany. 1992, vol. 32, no. 2, str. 85–100.

¹Janja Zule

Inšitut za celulozo in papir Ljubljana Slovenia ²Gabriele Weinberger, Corinna Hentschke, PTS Papiertechnische Stiftung, München, Germany ³Ricardo Pereira, Alp Erguensel, TUHH, Technische Universität, Hamburg-Harburg, Germany ⁴Quentin Thiebaut, CELABOR SCRL, Herve, Belgium

