Intensification of „living machine” wastewater treatment

Summary of PhD thesis

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I. Introduction

Fix film and hybrid activated sludge/biofilm systems are widely used in advanced wastewater treatment. The immobilization of microorganisms has several advantages: higher degradation rates are available, the mass and age of biofilm are more controllable. Microorganisms fixed in biofilm are more resistant against toxic compounds and sudden changes in pollutants load than the suspended cells of activated sludge.

During my PhD research I studied correlation between physico-chemical characteristics and colonization properties of polymer fiber biofilm carriers. Carriers selected by their characteristics were tested during biofilm colonization experiments in a pilot plant scale wastewater treatment plant. During these experiments the initial and matural phase of biofilm colonisation and the effect of operating parameters on colonisation were studied.

Examination of cyclodextrin based sorbents developed for removal of micro-pollutants from biologically treated wastewater was also carried out. An analytical method for the determination of cyclodextrin content of the sorbents was developed. Based on these results a proposal was given for the optimal composition of the sorbents. In a pilot plant scale experiment the adsorption capacity of cyclodextrin polymer beads in respect of micro-pollutants was also studied in wastewater matrix.

II. Materials and methods

II.1 Physico-chemical characterisation of biofilm carriers and their application in pilot plant scale biofilm colonisation experiments

Morphological characteristics, specific surface area, wettability, adsorption capacity and zeta potential of several polymer (polypropylene, carbon, nylon and polyester) fibers were studied. Amount of extractable organic matter of the polymer fibers was also measured during sample preparation washing processes.

Based on the results of physico-chemical measurements four types of polymer fibers were selected and tested in biofilm colonisation experiments carried out in the pilot plant scale wastewater treatment plant of Organica Ecotechnological Development Centre. The pilot plant scale wastewater treatment plant consisted of eight cascade reactors each having a volume of 2 m^3. The system operated with mechanically pretreated municipal wastewater. On the top of the reactors plants were placed and their roots were functioning as natural biofilm carriers. In the lower parts of the reactors, which was not available for the roots of the plants,

polymer fibers were placed to provide artificial surface for biofilm development. Reactors were aerated applying ceramic fine distributors.

During the four colonization experiments changes in the quality of raw wastewater and the water of the reactors was continuously studied. Temperature, pH, total and dissolved chemical oxygen demand (COD), total suspended solids (TSS), total nitrogen (TN), concentration of ammonium-, nitrite- and nitrate-ions were measured in every second or third day. Change of dissolved oxygen concentration was continuously recorded by sensors.

Dry and organic matter content and specific dehydrogenase enzyme activity of the biofilms grown on polypropylene and polyester carriers were studied, too. Total enzyme activity was calculated based on the biofilms' specific enzyme activity and dry matter content data.

Micromorphology of the biofilms was studied by scanning electron microscopy. Examination of bacterial communities in the biofilm was carried out applying T-RFLP (terminal restriction fragment length polymorphism) method in the Department of Microbiology. In case of a few samples pyrosequencing was also used to get information about the taxa of the biofilm.

II.2 Experiments for removal of micro-pollutants from biologically treated wastewater

During my experiments beta-cyclodextrin cross-linked by epichlorohydrin (Cyclolab Ltd., Hungary) and cyclodextrin based, sintered nanofilters (Bay Zoltán Applied Research Nonprofit Ltd., Hungary) were applied as sorbents. The studied nanofilters were manufactured in various compositions: they had different cyclodextrin and additive material content and different thickness. The aim of my experiments was the examination of the stability, extractable matter content, sorption capacity and regenerability of the nanofilters. Adsorption capacity was studied applying three model compounds (ibuprofen, carbamazepine and rhodamine-B). Adsorption was followed by total organic carbon (TOC) measurements in case of ibuprofen and carbamazepine, and by spectrofluorimetry in case of rhodamine-B.

For the removal of the pollutants originating from the manufacturing process, a sample preparation washing process was developed to avoid uncontrollable influences on the adsorption experiments. A method was elaborated for the regeneration of the nanofilters with ethanol solution, too. The steps of sample preparation washing process and the removal of the solvent after the regeneration process were controlled by TOC measurements.

The sorption capacity of the cyclodextrin polymer beads was studied in wastewater deriving from the above mentioned pilot plant scale wastewater treatment plant. Solution of drugs was

added to the filtered wastewater and the sorption capacity of the sorbents was studied under dynamic conditions in a sorption column. The dynamic sorption experiments were carried out with cyclodextrin polymer beads, activated carbon and the mixture of the two sorbents. The rate of sorption was also studied when the two sorbents were layered on each other.

After the laboratory scale sorption measurements pilot plant scale experiments were also performed. Nine micro-pollutants (ibuprofen, ketoprofen, naproxen, diclofenac, bisphenol-A, ß-estradiol, ethynil estradiol, estriol and cholesterol) were added to the biologically treated, filtered wastewater and cyclodextrin polymer beads were applied as sorbents. The concentration of the biologically treated wastewater, the filtered wastewater, the wastewater spiked with the nine micro-pollutants and the wastewater samples collected after different contact times were analysed by gas chromatography-mass spectrometry in the Laboratory of Enviromental Chemistry and Bioanalytics.

III. New scientific results

1. Characterisation of the biofilm carrier material

1.1 Based on the results of pilot plant scale experiments carried out beside fluctuating organic matter load and changing hydraulic load, I determined that among several polypropylene and polyester carriers the biofilms grown on the polypropylene sample – having 33 μm filament diameter, 3000 dtex linear density and 6.4 g/dtex elongation at break – had the highest dry matter content and total enzyme activity.

1.2 During the examination of the effect of polypropylene carriers' surface properties on biofilm colonization, I identified the wettability and the roughness as main influencing factors during biofilm colonization on polymer fiber based carriers.

2. Variations of water quality in a pilot plant scale „living machine" wastewater treatment plant

2.1 I recognized that the parts of the pilot plant scale wastewater treatment plant consisting of eight cascade reactors are separable according to their function during wastewater treatment. While in the first three reactors degradation of organic matter, removal of suspended solids and conversion of ammonium-nitrogen are the main processes, in the other five reactors nitrification processes are dominant.

2.2 Comparing the results of the four colonisation experiments in the pilot plant scale wastewater treatment plant, I recognized that beside 2.5 m^3 day^{-1} m^{-3} specific hydraulic load about 70% total COD removal, 60% total nitrogen removal are avalaible and the efficiency of nitrification is more than 90%, if the pollutant load does not exceed the following values: 900 O_2 g day^{-1} m^{-3} total COD (400 O_2 g day^{-1} m^{-3} dissolved COD) and 120 g day^{-1} m^{-3} (within this 75 g day^{-1} m^{-3} NH_4-N) total nitrogen.

3. Studying biofilm colonization in a "living mashine" type pilot plant scale wastewater treatment plant

3.1 I accomplished specific enzyme activity measurements of biofilms grown on polymer fiber carriers with an own optimised method based on a previously applied one for activated sludge.

3.2 I found that there are no significant changes in dry matter content and diversity indexes of biofilms after 14 days, so this time is enough to reach the matural

phase of biofilm formation in the pilot plant scale „living machine” wastewater treatment plant.

3.3 I justified that a functional separation of the reactors in the pilot plant scale wastewater treatment plant is also observable in the characteristics of the biofilms grown on the carriers placed into different reactors. In those reactors, where degradation of organic matter, removal of suspended solids and conversion of the ammonium-nitrogen are the main processes, larger amount of biofilm grew having also higher total enzyme activity than in those, where nitrification processes are dominant.

3.4 During the examination of temporary oxygen deficiency I recognized that the cascade system construction has advantages in case of sudden changes of operating parameters. In the last (eighth) reactor there were no significant differences in the dry matter content and the composition of the bacterial community (studied by T-RFLP method) of the biofilm between the status before and after the breakdown.

4. Examination of cyclodextrin containing sorbents developed for removal of micro-pollutants from biologically treated wastewater

4.1 I developed a static sorption based method for the determination of cyclodextrin content of high density polyethylene and cyclodextrin containing, sintered sorbents. The static sorption was carried out with defined sorbent/ model compound ratio, where the model compounds were ibuprofen and carbamazepine and the adsorption was followed by TOC concentration measurement of the solution phase.

4.2 I justified that the optimal cyclodextrin polymer bead content of the sintered sorbents is 30 m/m%.

4.3 I determined that reduction of thickness and addition of structure modifying materials increase the specific adsorption capacity of sintered sorbents.

4.4 Ammonium bicarbonate was the best among the structure modifying compounds. Sintered sorbents manufactured with this material had the highest specific adsorption capacity based on the results of measurements applying ibuprofen as a model compound.

4.5 I justified that the cyclodextrin containing, sintered sorbents can be regenerated, and their specific adsorption capacity does not change during five sorption and regeneration cycles.

4.6 Pilot plant scale experiments, aiming removal of micro-pollutants added in concentration having the order of magnitude typical in the biologically treated wastewater and applying beta-cyclodextrin polymer beads as sorbents for post-purification of wastewater, showed that the beta-cyclodextrin polymer bead is appropriate for adsorbing the biologically not degradable diclofenac with 85% efficiency.

IV. List of scientific publications

Papers directly related to the PhD thesis

1. L. Jurecska, K. Barkács, É. Kiss, G. Gyulai, T. Felföldi, B. Törő, R. Kovács, Gy. Záray: Intensification of wastewater treatment with polymer fiber-based biofilm carriers, Microchem. J. 107 (2013) 108-114.
   DOI: 10.1016/j.microc.2012.05.028; IF=3.58
2. L. Jurecska, P. Dobosy, K. Barkács, É. Fenyvesi, Gy. Záray: Characterization of cyclodextrin containing nanofilters for removal of pharmaceutical residues, J. Pharm. Biomed. Anal. 98 (2014) 90-93.
   DOI: 10.1016/j.jpba.2014.05.00; IF=2.82
3. T. Felföldi, L. Jurecska, B. Vajna, K. Barkács, J. Makk, G. Cebe, A. Szabó, Gy. Záray, K. Márialigeti: Texture and type of polymer fiber carrier determine bacterial colonization and biofilm properties in wastewater treatment, Chem. Eng. J. 264 (2015) 824-834.
   DOI: 10.1016/j.cej.2014.12.008; IF=4.05

Research reports directly related to the PhD thesis

1. L. Jurecska, K. Barkács, E. Gombos, Gy. Záray: Különböző víztípusok xenobiotikum tartalmának eltávolítása, az eltávolítási eljárások szakirodalmi áttekintése (ELTE, Budapest, 2009)
2. É. Kiss, L. Jurecska, G. Gyulai, K. Barkács, Gy. Záray: Műanyag és műanyagalapú szálak alkalmazási lehetőségei a szennyvíztisztításban. A szálak fizikai-kémiai jellemzése (ELTE, Budapest, 2010)
3. L. Jurecska, K. Barkács, Gy. Záray: Szintetikus alapú, nagy fajlagos felületű biofilm hordozók fizikai-kémiai tulajdonságainak meghatározása és baktériumok kolonizációja szempontjából kedvező módosítása (ELTE, Budapest, 2010)

4. E. Gombos, L. Jurecska, K. Barkács, Gy. Záray: Xenobiotikumok eltávolítására alkalmazható alternatív fizikai-kémiai eljárások áttekintő értékelése (ELTE, Budapest, 2010)
5. K. Barkács, I. Varga, L. Jurecska, Gy. Záray: Ciklodextrin tartalmú szűrők összetételének jellemzésére végzett fizikai-kémiai vizsgálatok adatai (ELTE, Budapest. 2010)
6. K. Barkács, I. Varga, Gy. Záray, L. Jurecska: Fizikai-kémiai módszerek kidolgozása ciklodextrin tartalmú szűrők stabilitásának, kapacitásának és regenerálhatóságának jellemzésére (ELTE, Budapest, 2010)
7. K. Barkács, Gy. Záray, L. Jurecska, I. Varga: Ciklodextrin tartalmú mintavevő szűrők vízközegekben való alkalmazhatóságának jellemzése fizikai-kémiai vizsgálatokkal (ELTE, Budapest, 2010)
8. K. Barkács, Gy. Záray, L. Jurecska: Ciklodextrin hatóanyagú szűrőkkel dinamikus körülmények közt víztisztítási céllal végzett laboratóriumi kísérletek (ELTE, Budapest, 2010)
9. K. Barkács, Gy. Záray, L. Jurecska: Ciklodextrin hatóanyagú szűrők technológiai paramétereinek optimálását célzó laboratóriumi szorpciós kísérletek (ELTE, Budapest, 2010)
10. K. Barkács, L. Jurecska, P. Dobosy, I. Molnár-Perl, N. Andrási, I. Varga, Gy. Záray: Ciklodextrin tartalmú szűrők fizikai-kémiai vizsgálata (ELTE, Budapest, 2011)
11. K. Barkács, E. Gombos, L. Jurecska, I. Molnár-Perl, N. Andrási, A. Vasanits-Zsigrai, Gy. Záray: A CD-FILTER projekt keretében Telkiben végzett félüzemi kísérletekhez kacsolódó fizikai-kémiai vizsgálatok (ELTE, Budapest, 2011)
12. N. Andrási, K. Barkács, G. Cebe, P. Dobosy, L. Jurecska, K. Márialigeti, I. Molnár-Perl, B. Vajna, Gy. Záray, A. Vasanits-Zsigrai: Szintetikus alapú, nagy fajlagos felületű biofilm-hordozók baktérium kolonizációjának vizsgálata félüzemi kísérleti rendszerben (ELTE, Budapest, 2011)
13. K. Barkács, L. Jurecska, P. Dobosy, Gy. Záray: Szintetikus alapú, nagy fajlagos felületű biofilm-hordozók baktérium kolonizációjának vizsgálata félüzemi kísérleti rendszerben (ELTE, Budapest, 2012)

Oral presentations directly related to the PhD thesis

1. L. Jurecska, K. Barkács, É. Kiss, T. Felföldi, B. Törő, R. Kovács, Gy. Záray: Intensification of wastewater treatment with polymer fiber-based biofilm carriers, XIV. Hungarian-Italian Symposium on Spectrochemistry, Sümeg, October 5-7, 2011
2. L. Jurecska, K. Barkács, É. Fenyvesi, E. Andersen, Gy. Záray: Mikro-szennyezők eltávolítása ciklodextrin tartalmú szorbensekkel, II. MaSzeSz Junior Szimpózium, Budapest, December 9, 2011

3. L. Jurecska, K. Barkács, B. Törő, R. Kovács, Gy. Záray: Biofilm kolonizáció vizsgálata műszál alapú hordozókon, Környezettudományi Doktori Iskolák Konferenciája, Budapest, August 30-31, 2012
4. P. Dobosy, L. Jurecska, K. Barkács, É. Fenyvesi, E. Andersen, Gy. Záray: Vizek mikro-szennyezőinek eltávolítására kifejlesztett nanoszűrők szorpcióképes ciklodextrin tartalmának vizsgálata, Környezettudományi Doktori Iskolák Konferenciája, Budapest, August 30-31, 2012
5. L. Jurecska, K. Barkács, P. Dobosy, É. Fenyvesi, E. Andersen, Gy. Záray: Removing micro-pollutants from wastewater applying cyclodextrin based nanofilters, IWA 4th Eastern European Young Water Professionals Conference, Szentpétervár, October 4-6, 2012
6. L. Jurecska, K. Barkács, P. Dobosy, R. Lőcsei, B. Törő, R. Kovács, Gy. Záray: Mesterséges hordozók vizsgálata félüzemi élőgépes szennyvíztisztító rendszerben, I. Környezetkémai Szimpózium, Mátraháza, October 11-12, 2012
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8. P. Dobosy, L. Jurecska, K. Barkács, É. Fenyvesi, E. Andersen, Gy. Záray: Vizekben lévő mikro-szennyezők eltávolítására kifejlesztett nanoszűrők megkötőképes ciklodextrin tartalmának meghatározása, II. Környezetkémiai Szimpózium, Dobogókő, October 10-11, 2013

Poster presentations directly related to the PhD thesis

1. L. Jurecska, K. Barkács, Gy. Záray, É. Fenyvesi, E. Andersen, I. Rácz, L. Szente: Felületmódosított hordozók ciklodextrin tartalmának meghatározása szorpciós vizsgálatokkal, MKE I. Nemzeti Konferencia, Sopron, May 22-25, 2011
2. L. Jurecska, B. Törő, T. Felföldi, K. Barkács, R. Kovács, Gy. Záray: Polymer based biofilm carriers for improving the efficiency of biological wastewater treatment, Chinese-European Cooperation for a Long Term Sustainability, Budapest, November 10-11, 2011
3. L. Jurecska, K. Barkács, P. Dobosy, É. Fenyvesi, E. Andersen, Gy. Záray: Vizekben előforduló xenobiotikumok eltávolítására kifejlesztett ciklodextrin tartalmú szűrőlapok vizsgálata, ELTE Innovációs Nap, Budapest, February 23, 2012
4. P. Dobosy, K. Barkács, L. Jurecska, É. Fenyvesi, E. Andersen, Gy. Záray: Mikro-szennyezők eltávolítására kifejlesztett, ciklodextrinnel módosított szűrők vizsgálata, ELTE Bolyai Konferencia, Budapest, May 4, 2012
5. L. Jurecska, K. Barkács, T. Felföldi, G. Cebe, B. Törő, R. Kovács, Gy. Záray: Physico-chemical characterization of polymer-fiber based biofilm carriers and their

application in wastewater treatment, 6th International Conference for Young Water Professionals, Budapest, July 10-13, 2012

6. L. Jurecska, K. Barkács, Gy. Záray, L. Jicsinszky, E. Oláh, É. Fenyvesi: Methods for determining cyclodextrin content of modified textiles, XXIII IFATCC (International Federation of Associations of Textile Chemists and Colourists) Congress, Budapest, May 8-10, 2013

Popular science article directly related to the PhD thesis

1. L. Jurecska: Új típusú szűrők gyógyszermaradványok eltávolítására – Víztisztítás ciklodextrinekkel, Élet és Tudomány 3 (2012) 73-75.

Papers directly not related to the PhD thesis

1. I. Máthé, A. K. Borsodi, E. M. Tóth, T. Felföldi, L. Jurecska, G. Krett, Zs. Kelemen, E. Elekes, K. Barkács, K. Márialigeti: Vertical physico-chemical gradients with distinct microbial communities in the hypersaline and heliothermal Lake Ursu (Sovata, Romania), Extremophiles 18:3 (2014) 501-514.
   DOI: 10.1007/s00792-014-0633-1, IF: 2.17

2. A. K. Borsodi, T. Felföldi, I. Máthé, V. Bognár, M. Knáb, G. Krett, L. Jurecska, E. M. Tóth, K. Márialigeti: Phylogenetic diversity of bacterial and archaeal communities inhabiting the saline Lake Red located in Sovata, Romania, Extremophiles 17:1 (2013) 87-98.
   DOI: 10.1007/s00792-012-0496-2, IF: 2.17

3. M. Varga, J. Dobor, A. Helenkár, L. Jurecska, J. Yao, Gy. Záray: Investigation of acidic pharmaceuticals in river water and sediment by microwave assisted extraction and gas chromatography-mass spectrometry, Microchem. J. 95:2 (2010) 353-358.
   DOI: 10.1016/j.microc.2010.02.010, IF: 3.58