

Topics in Water Chemistry and Water Technology

2015

Annual Report of the Chair of Water Chemistry and Water Technology
and the DVGW Research Laboratory at the Engler-Bunte-Institut

ENGLER-BUNTE-INSTITUT



Dear colleagues and friends,

2015 is for sure the year of consolidation. Personally, my last four years in this new position seemingly passed by with an extremely high velocity. People joined our group and have already left the group to move into new positions. Among them, Susanne Lackner was appointed full professor at the Bauhaus-Universität in Weimar 2015, congrats!

Four new PhD students started their PhD projects this year. The question on what is going on at interfaces (i.e. biofilms) is the main topic which will be addressed in their projects. Productive biofilms will be cultivated in flow cells, and membrane biofilm reactors will be used to transform hydrogen to methane. Furthermore, membrane treatment and the question on how to measure concentration polarization will be an issue in the next years. Additionally, Marius Majewsky succeeded twice in our research field water quality: First of all, we could buy a DFG financed LC-MS/MS for our work on micro pollutants in aquatic systems. Secondly, he won a DFG project on sulfonamides and their potential metabolites.

Postdoctoral researchers from China and Nepal joined our group in 2015. Our postdocs and PhD students attended national and international conferences and workshops. Two PhD students were on short research stays abroad. The ABC (advanced biofilm course) was held at TU Delft this year. The course was overbooked and therefore still seems to be highly attractive after 10 years.

In March this year, I was appointed speaker of the Water Research Network Baden-Württemberg. The network is supposed to bring together researchers from universities in Baden-Württemberg. Beside three joint research projects, which are financed for 5 years, the network will organize workshops and conferences, which hopefully will further trigger the collaboration in the field of water research in Baden-Württemberg. The office of the network is directly located at our chair and Ulrike Scherer will be responsible for the administration and organization (see her report in this issue).

In October this year, we had an Alumni meeting with Doctors and Professors who worked for a while in our group in Munich and/or Karlsruhe. Reports from real life jobs in consulting companies on the one hand and universities on the other hand were extremely interesting to those who are short before leaving us. Thanks to all the Alumni who joined and made this day really unforgettable.

Enjoy this report and maybe pick one or the other idea for your own research.

My best wishes for 2016

Harald Horn

Mainstream Anaerobic Ammonium Oxidation (MAnAmO)



Susanne Lackner



Shelesh Agrawal



Samuel Welker

The harm of excessive nitrogen loadings to water bodies is well known (e. g. eutrophication). Among available technologies for removal, the partial nitrification-anammox process (PN-A) has become more and more important since its discovery in the 1990s, due to its large energy saving potential. By applying these bacteria in waste water treatment, up to 60 % energy reduction can be obtained compared to conventional removal technologies (e. g. nitrification-denitrification).

Recent research indicates that PN-A is possible even under mainstream conditions where it has to cope with lower temperatures, higher availability of organic carbon, and lower ammonium concentrations, compared to sidestream applications. Even though the general feasibility of PN-A processes under the mentioned difficult conditions has been shown, many questions remain.

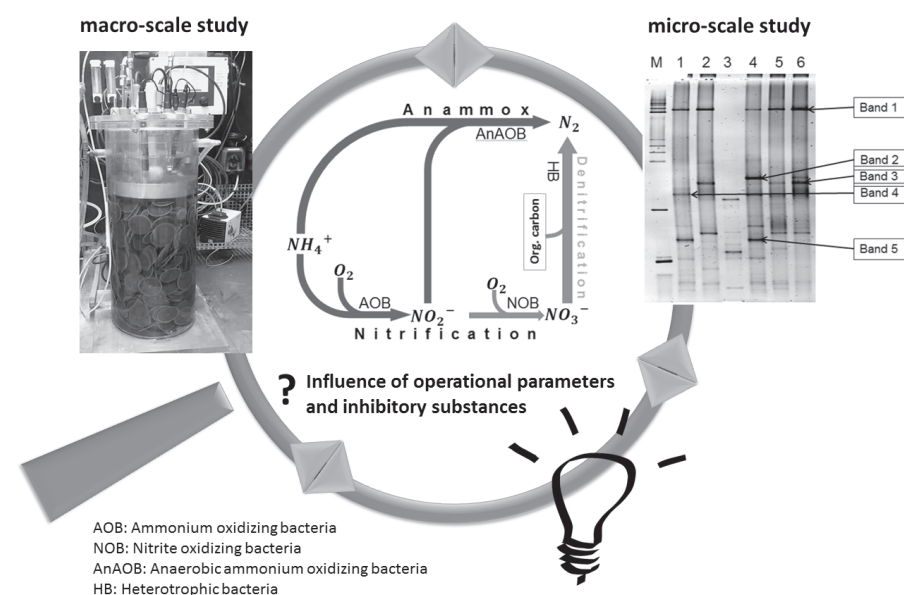
In this context, this year's research focus of our group has been mainly on investigating the influence of several operation parameters (e. g. substrate and dissolved oxygen concentration) on PN-A performance, as well as on gaining a better understanding of potentially inhibitory effects on the PN-A process (e. g. particulate matter and organic carbon).

These studies were carried out by operating three different reactor systems in lab-scale (sequencing batch reactors (SBR), moving bed biofilm reactors (MBBR), and hybrid (biofilm and suspended biomass) systems), and comparing performance and molecular biology analyses to also better understand processes on the micro-scale.

Current results indicate an inhibitory effect of organic carbon on the partial nitrification process, whereas the presence of particulate matter seems to influence mainly the second part of the PN-A process (anammox bacteria).

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Schematic representation of the anammox research at the institute.

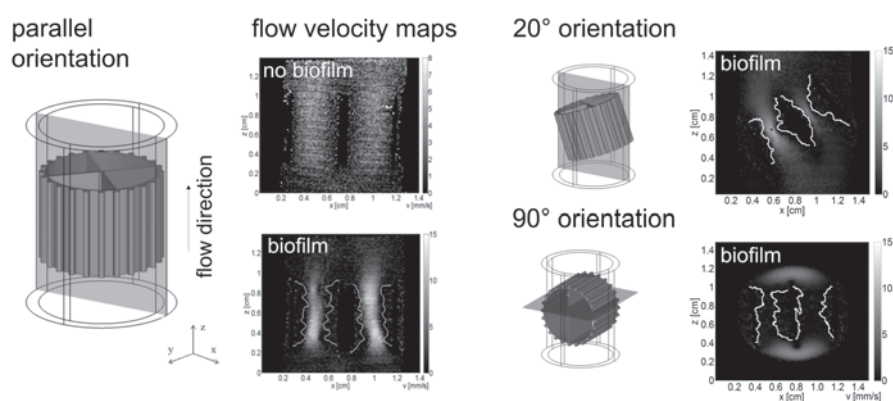
Determining the Flow Regime in a Biofilm Carrier by means of Magnetic Resonance Imaging

Being omnipresent in natural as well as in technical systems, biofilms show various structures with smooth, rough, fluffy, porous or compact texture. The structure of biofilms strongly influences the local flow field and mass transport of the substrates. The interaction between the biofilm matrix and the bulk phase is mainly driven by diffusion and advection, which play a key role for the metabolic activity. In this context, magnetic resonance imaging has proved to be the ideal tool for non-destructive and in-situ imaging of living biofilms and has a strong potential in biofilm research. With the aim to determine the flow regime in a carrier based biofilm used for waste water treatment, a plastic carrier with and without biofilm was exposed to a flow rate of 0.64 mm/s in a flow cell, see experimental set-up in the figure. Flow velocity maps reveal that the local flow velocities are significantly increased in the presence of the biofilm compared to the clean carrier. High flow velocities are found in the centre line, which drop towards the biofilm surface (biofilm surface indicated by white line). Within the biofilm matrix, no fluid flow was detected. There is a shift to higher flow velocities: the mean flow velocity was 2.4 mm/s and 4.3 mm/s in the carrier without biofilm and with biofilm, respectively. Additionally, different biofilm carrier orientations (parallel, 20° and 90°) to the upstream flow angle were investigated (see figure). A carrier orientation of 20° to the upstream flow angle leads to a 10 % increase of the mean flow velocity compared to parallel orientation due to the forced flow through the carrier. At an orientation angle of 90°, regions of stagnation were formed where almost no fluid exchange was observed. Consequently, diffusion was the predominant process for the transport of solutes. Unique data is created which enable analysis of mass transport in real biofilms and provide input data to verify mathematical simulations.



Maria Pia Herrling

Susanne Lackner



Local flow velocity measurements in two sections of a biofilm carrier (set-up): 2D flow velocity maps of a carrier without biofilm and with biofilm (biofilm surface is highlighted as a white line) were acquired for different carrier orientations (parallel, 20° and 90° to the upstream flow angle). The vertical color bar encodes the flow velocity v_z in mm/s. The applied flow rate was 0.64 mm/s in z-direction. The carrier has a diameter of 9 mm.

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Interaction of Biofilm Systems and Suspended Solids

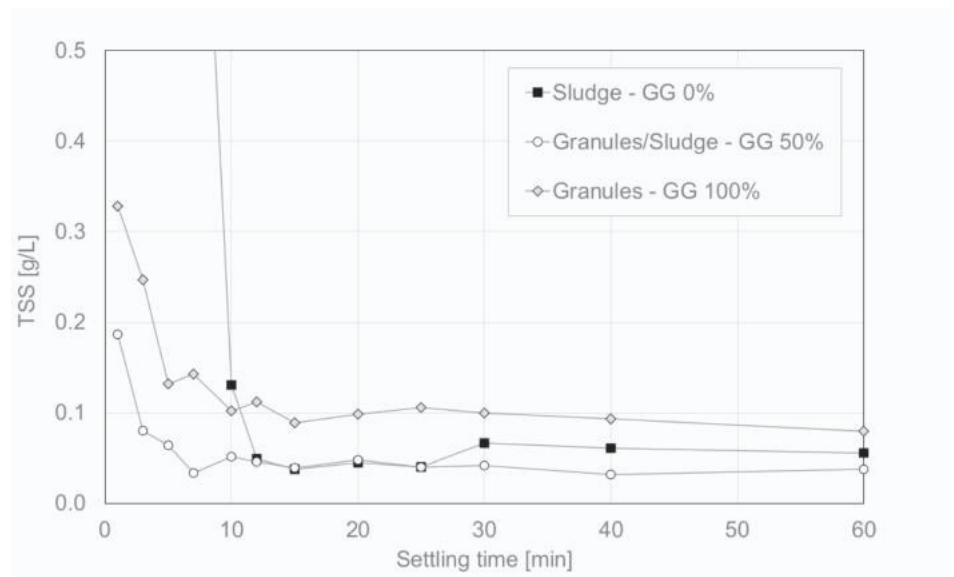


Fabian Brunner
Susanne Lackner

Biological waste water treatment worldwide is dominated by the activated sludge process. Within the last ten years, biofilm systems, especially aerobic granules, have entered the market. Besides their unique ability for simultaneous C, N and P removal in a single sequencing batch reactor (SBR) with high biomass concentration, a key advantage of aerobic granule systems is a significantly reduced settling time compared to activated sludge systems. However, there is still some work to do: Research of Rocktäschel et al. (2015) indicated that a increasing granulation grade (GG) within aerobic granular reactors ($m_{\text{granules}}/m_{\text{total biomass}}$) leads to higher concentrations of total suspended solids (TSS) in the effluent.

To investigate this further, initial experiments with aerobic granules collected from a granular sludge reactor and with suspended sludge from a waste water treatment plant were conducted. In batch tests resembling a reactor cycle of the granular sludge reactor, different granulation grades were investigated by mixing granules (\varnothing 2 - 5 mm) and activated sludge. A high amount of real waste water particles (45 - 100 μm) were added to the synthetic substrate for the reactor operation to achieve a TSS concentration in the influent of 0.5 g/L. During the settling, after the end of the aeration, the TSS concentration at a certain point in the reactor was determined via turbidity measurements. Results of these experiments are shown in the figure. As can be seen in the figure, the TSS concentration is highest after 12 min of settling if only granules (GG 100 %) are present within the reactor. This is due to a lower surface area and partly smoother surface structure of the granules compared with activated sludge. The experiments will help to better understand the removal of suspended solids by aerobic granules in sequencing batch reactors.

Reference: Rocktäschel et al., 2015. *Sep. Purif. Technol.* 142, 234-241.



Development of total suspended solids concentration within the first 60 minutes settling time.

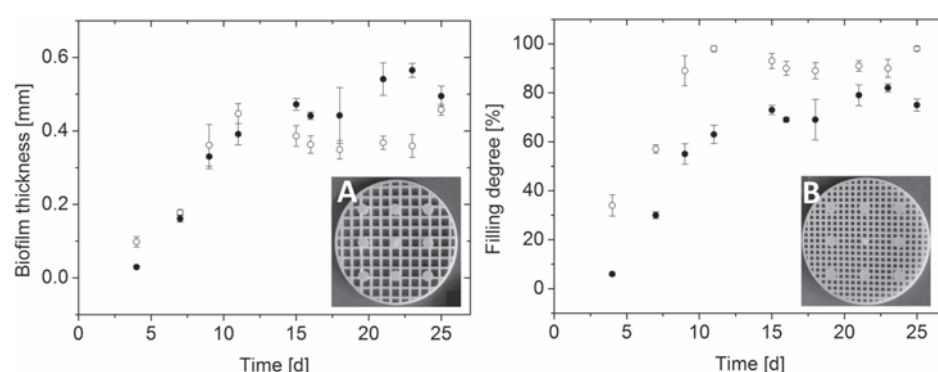
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Comparison of Biofilm Structure on Different Carriers Used in Lab-Scale Moving Bed Biofilm Reactors

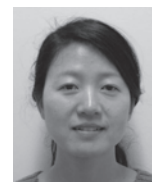
Various types of carriers with different geometries are available on the market for the use in moving bed biofilm reactors (MBBRs). Independent of their geometry it is promised that those carriers favor the growth of biofilms with a high content of active biomass. To date, there has been no study investigating biofilm structure development on the carriers and the influence of carrier geometry on the structure of the growing biofilm.

This study aimed at characterizing the structure of biofilms developing on carriers used in lab-scale MBBRs by means of optical coherence tomography (OCT). Two types of carriers were compared (see figure). 3D OCT images were acquired regularly, which allowed tracking of biofilm growth on the carriers. The biofilm structure and accumulation were characterized with respect to biofilm thickness (L_f) and compartment filling degree (η).

The figure illustrates the development of biofilm (L_f and η) on both carriers throughout the experiment. Both carriers showed similar trends of increasing biofilm thickness L_f and compartment filling degree η with ongoing cultivation. Nevertheless, at the beginning of the experiment, carriers B had slightly higher values for L_f and η compared to carriers A, which suggested that carrier B promotes quicker initial establishment of biofilm. After the compartments of carriers B were filled with biofilm on day 11, the biofilm thickness on carriers A continued to increase and surpassed that of carriers B. The compartment filling degree η of carriers B was always higher than that of carriers A, indicating that the compartments of carriers A were not fully filled with biofilm until the end of the reactor operation. Carriers B with smaller compartment size promoted quick initial biofilm formation, whereas carriers A with larger compartment size accumulated more biofilm in terms of biofilm volume.



Biofilm structure development on carrier A (●) and B (○) with respect to mean biofilm thickness L_f and compartment filling degree η . The two carriers have a diameter of 30 mm and a thickness of 1.05 mm. Carrier A has 103 compartments ($2.4 \times 2.4 \text{ mm}^2$). Carrier B has 300 compartments ($1.4 \times 1.4 \text{ mm}^2$).



Chunyan Li



Michael Wagner

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Investigating biofilm
structure developing on
carriers from lab-scale
moving bed biofilm reactors
based on light microscopy
and optical coherence
tomography. Bioresource
Technology, 200, 128-136.

Operating a Microbial Fuel Cell (MFC) with Municipal Waste Water to Generate Electrical Power



Dominic Breitkopf

Michael Wagner

The Federal Ministry of Education and Research (BMBF) is funding the BioBZ project, which aims to install optimized microbial fuel cells (MFC) on a municipal waste water treatment plant (WWTP) to generate electrical energy by the anaerobic degradation of carbon sources as well as to test the suitability of MFCs to remove micropollutants found in waste water.

In 2015, the experimental setup for the simultaneous operation of up to four BioBZ was installed at the Chair of Water Chemistry and Water Technology. Focus has been laid on the flow velocity of the waste water through the MFC as well as on the structure of the growing biofilm. In an initial experiment, one MFC was operated in flow-through mode with mechanically cleaned municipal waste water collected at the nearby WWTP Neureut. For 192 days, the carbon utilization was quantified based on the chemical oxygen demand (COD) as well as on the electrical power produced.

The figure reveals the development of the biofilm on the anode. During this period, the inflow COD was ≥ 50 mg/L O_2 , which decreased over time due to the degradation in the storage tank before refilling. The growth of biofilm led to a certain power production, which reached about 50 mW/m^2 of anode area after 190 days of operation. A peak in the power production was determined at day 170, showing the potential of the BioBZ MFC to produce about 200 mW/m^2 when operated with municipal waste water. Experiments at elevated flow velocities were performed to control the biofilm thickness and improve the power output. Higher flow velocities reduce the boundary layer thickness above the biofilm surface and, thus, increase the power production. However, when biofilm detachment occurs, the power output may also drop. Hence, fluctuations of the flow velocity impact the overall performance of MFCs. Future experiments will investigate the effect of this parameter in more detail. Especially, biofilm visualization by means of optical coherence tomography will help to relate the power output to the biofilm structure as well as the cultivation conditions.

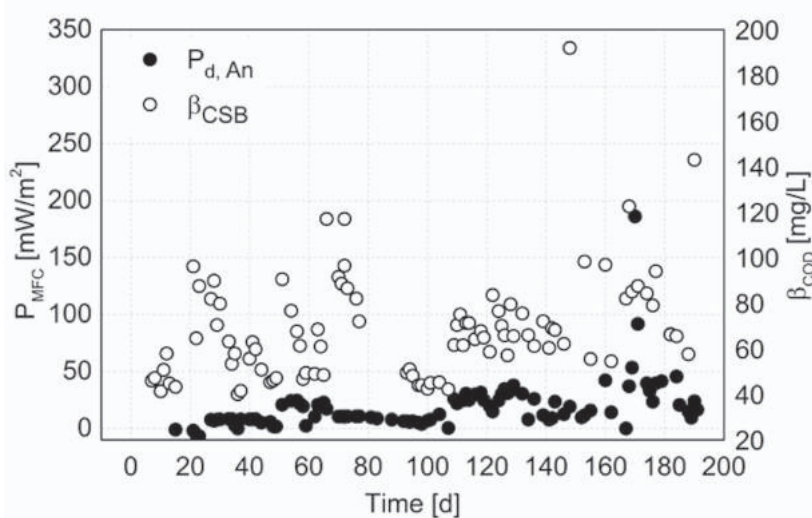
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Germany

For further details see:
www.bio-bz.de



Inflow COD of the waste water used to feed the BioBZ microbial fuel cell as well as the electrical power produced over the experimental duration of 192 days.

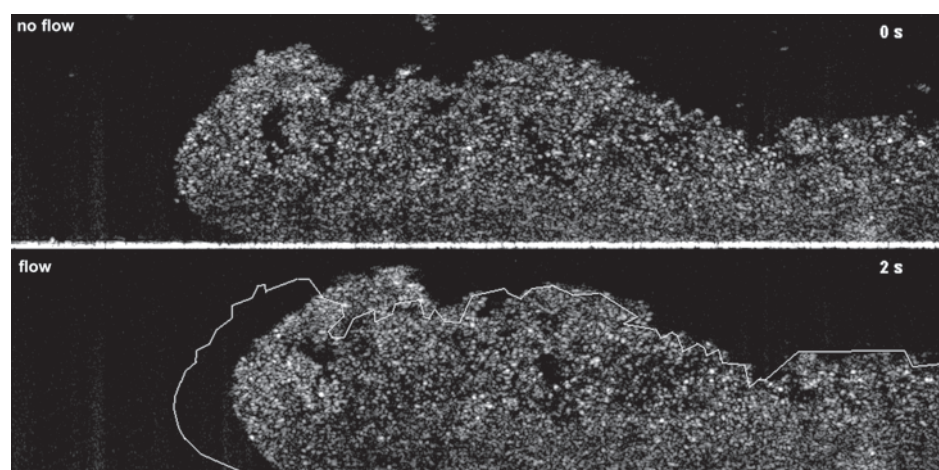
Time-Resolved Biofilm Deformation Experiments Showing Elastic and Viscoelastic Behaviour of Biofilms

The investigation of fluid-structure interactions is an important field in biofilm research. Information about material properties together with the applied forces will help to understand and shape the biofilm structure, to improve turnover rates, and in case of microbial fuel cells, enhance the electrical power output.

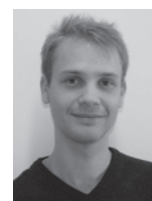
The scale on which fluid-structure interactions are relevant is the mesoscale (mm-scale). A technique capable visualizing structures of several mm³ at a high resolution of a few μm is optical coherence tomography (OCT).

OCT has several great advantages to visualize biological samples over other imaging techniques: no staining necessary, non-invasive, and in situ. Moreover, OCT acquires images really fast. Optical cross sections through the biofilm structures can be acquired within milliseconds, whole volumetric representations in seconds. This allows to measure either dynamic or time-lapsed deformation processes. In dynamic deformation experiments, data is acquired so fast that the series of cross sections provides 'real-time' information about the deformation behaviour. Time-lapsed experiments on the other hand determine three-dimensional structural changes of biofilm (i. e., a patch) over time in the range of minutes, hours, or even days. It is therefore possible to investigate two different deformation processes: elastic and viscoelastic deformation as a result of applied shear stress.

In elastic deformation, the biofilm regains the original structure, while in viscoelastic deformation some of the applied energy irreversibly deforms the biofilm. With the established approach, we found quantities for the material properties of the shear modulus $G = 27 \text{ Pa}$, describing the rigidity, and the Young's modulus $E = 36 \text{ Pa}$, a measure of elasticity. Moreover, we could link a change of biofilm porosity to both of the processes, showing a decrease of porosity by 2 % during the elastic deformation, whereas in viscoelastic deformation experiments the porosity changed by more than 5 %.



OCT cross sections through the biofilm structure. The top row shows the biofilm structure before flow was started and hence no shear stress was applied. The bottom row displays the biofilm after two seconds of flow. The present shear stress caused biofilm structure to deform. The white outline represents the initial, undeformed biofilm structure. The scale bar equals 250 μm and flow is from the left to the right.



Florian Blauert

Michael Wagner

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Wagner, M., 2015. Time-
resolved biofilm deformation
measurements using optical
coherence tomography.
Biotechnology
Bioengineering 112 (9),
1893-1905.

For further details see:
[https://blogit.itu.dk/
evoblissproject/](https://blogit.itu.dk/evoblissproject/)

Effect of the Daily Temperature Cycle on the Biofilm Formation and Composition in Micro-Fluidic Devices Mimicking Drippers



Jueying Qian

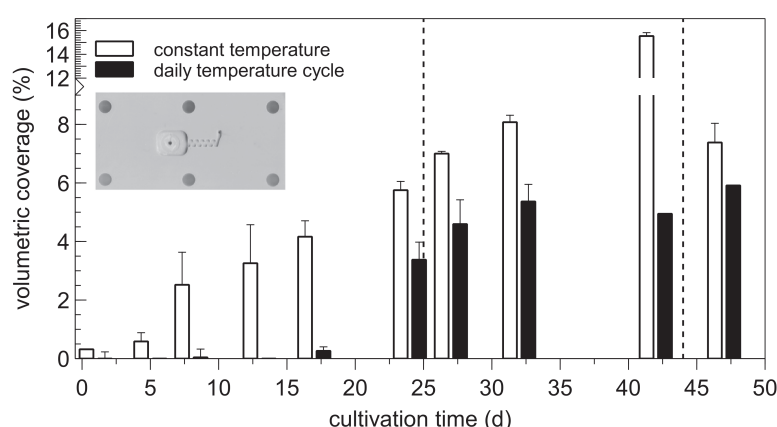
Michael Wagner

In Israel, treated waste water (TWW) is extensively used in drip irrigation as an efficient water solution. However, biofilm forms in the drip pipe, especially inside the drippers, which are necessary to assure a constant drip rate.

The objective of this study was to investigate the impact of the daily temperature cycle on the formation and composition of biofilm in drippers. The inner geometry of a dripper is copied in our 3D printed microfluidic devices (MFD). In order to mimic the temperature conditions in Israel, a lab-scale experimental setup was built (temperature box), simulating the daily temperature cycle between 20 °C (ambient temperature) and roughly 50 °C. MFDs were fed with secondary treated waste water from the waste water treatment plant Neureut (Germany). The biofilm formation inside the MFD was monitored and quantified over time non-invasively and in situ by means of optical coherence tomography (OCT).

Results show that biofilm formed faster at constant, ambient temperature (black bars) compared to the daily temperature cycle simulated inside the temperature box (see figure). Further, the chemical characterization of the biofilm showed a ratio of volatile solids (VS) to total solids (TS) of 79 ± 1.3 % (g VS/g TS), independent of the temperature condition. Extracellular polymeric substances (EPS) were extracted and classified into soluble (S-EPS), loosely bound (L-EPS) and tightly bound EPS (T-EPS). The amount of EPS was characterized as the sum of proteins and carbohydrates. At ambient temperature, 0.45 g EPS/g VS formed. Under changing temperature conditions, the amount of EPS was 0.31 g EPS/g VS with a higher content of S-EPS compared to biofilm grown at constant temperature.

The study combines MFDs for growing biofilms, OCT as imaging modality as well as the chemical characterization of the biofilm. The methodology is effective and helps revealing the formation of biofilm in drip irrigation systems. Especially, the effect of temperature on the biofilm formation was determined.



Fraction of the dripper geometry (MFD) covered with biofilm (volumetric coverage). Biofilm accumulation is reduced when the daily temperature cycle between 20 and 50 °C was simulated in the temperature controlled box. Between days 25 and 44, sodium acetate was added as additional substrate (period between dashed lines). The MFD has a dimension of 50 mm x 25 mm.

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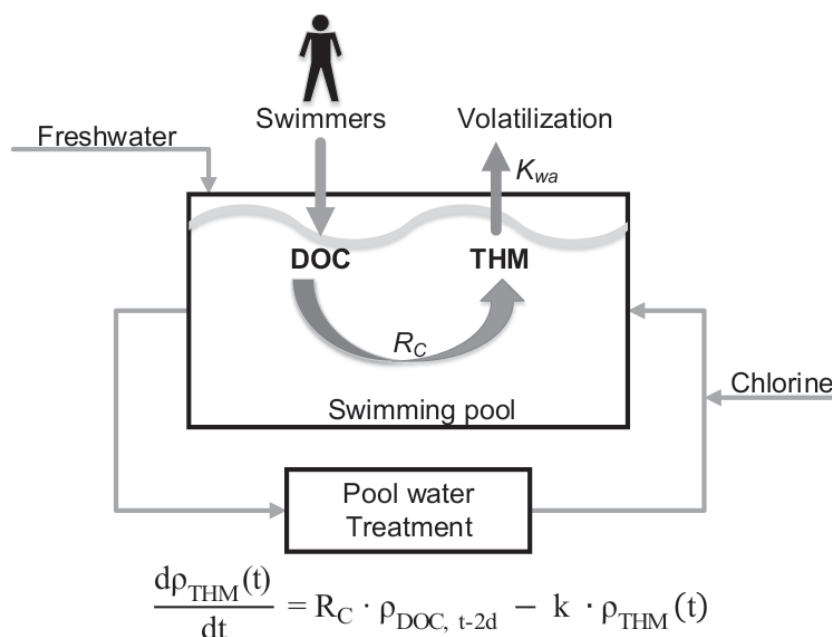
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Occurrence and Simulation of Trihalomethanes in Swimming Pool Water: A Simple Prediction Method based on DOC and Mass Balance

Water in public swimming pools is practically continuously disinfected in order to control the pathogenic microorganisms and to guarantee the health of swimming pool visitors. To date, chlorine-based chemicals are still the most commonly applied disinfectants, which react with organic and inorganic substances in pool water, producing health concerning disinfection by-products (DBP). Trihalomethanes (THM) are the most typical disinfection by-products (DBPs) found in public swimming pool water. The irregular contribution of substances from pool visitors and long contact time with disinfectant make the forecast of THM in pool water a challenge.

In this work, occurrence of THM in a public indoor swimming pool was investigated and correlated with the dissolved organic carbon (DOC). Daily sampling of pool water for 26 days showed a positive correlation between DOC and THM with a time delay of about two days, while THM and DOC did not directly correlate with the number of visitors. Based on the results and mass-balance in the pool water, a simple simulation model for estimating THM concentration in indoor swimming pool water was developed. Formation of THM from DOC, volatilization into air and elimination by pool water treatment were considered in the simulation. Formation ratio of THM gained from laboratory analysis using native pool water and information from the field study in an indoor swimming pool reduced the uncertainty of the simulation. The simulation was validated by measurements in the swimming pool for a further period of 50 days.

The simulation can be used to estimate THM concentration and its long-term accumulation trend under real indoor swimming pool water conditions with a reduced amount of data required. Additionally, the model can be useful in conducting health-related risk assessment concerning exposure to DBP and in estimating infrastructure needs for upgrading treatment facilities.



Sketch of the simulation for THM mass balance in swimming pool water.



Di Peng



Florencia Saravia

Gudrun Abbt-Braun

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Sustainable Management of Available Water Resources with Innovative Technologies (SMART-MOVE) - Brackish Water Usage



Oliver Jung

Florencia Saravia

Funding: Federal Ministry of
Education and Research
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Partners from Israel, Jordan,
Palest. Territories, Germany

The overarching aim of the BMBF founded SMART joint project, whose third phase started in February 2015, is to develop an integrated water resources management (IWRM) in the lower Jordan rift valley (LJRV). In the previous phase, the potential and challenges of an implementation of membrane technologies for the treatment of highly saline spring-, well- or ground waters on a local level have been studied on an innovative small scale pilot plant. Agricultural irrigation, ground water recharge and drinking water supply have been identified as possible application areas. Within the SMART-MOVE phase of the project, the project part of the EBI is to elaborate a conclusive handbook on brackish water treatment with membrane technologies, including technology analysis and planning of desalination plants as well as questions related to sustainability, i. e. brine disposal and waste management. In collaboration with key decision holders and with a focus on basic knowledge adapted to local conditions, the handbook should provide a work of reference and standards for brackish water desalination in semi-arid regions.



Marc Tuczinski

Florencia Saravia

Autogenerative Two-Phase High Pressure Fermentation (AG-HiPreFer)

High pressure fermentation would allow for a direct supply of the produced methane into the national gas grid. For this purpose, a fixed bed methane reactor can be operated under high pressure. The fixed bed has to be fed with a high concentrate influent containing volatile fatty acids as the best substrate for the methanotrophic bacteria. The feed stream can be produced by a thermophilic hydrolysis (55 °C) stage. Within the hydrolysis reactor, volatile organic acids (mainly acetic acid) can be produced from renewable energy crops like maize.

A well-known problem for such two stage solutions is the biomass separation after the hydrolysis step. The hydrolysis is typically operated at pH 6 and the methane reactor at a pH value of around 7. Within the project, microfiltration is used to separate the particulate material from dissolved organic components. Two main research questions have to be addressed: What is the achievable permeate flux and how will fouling influence the filtration performance?

Series of studies were performed to select the right type of membrane material by which high flux and low fouling could be achieved. Ceramic microfiltration membrane modules proved to be the best option to treat the effluent of the hydrolysis reactor (percolate). A range of pore sizes (0.2 - 0.8 µm) has been tested. The crossflow filtration tests showed a total organic carbon (TOC)-rejection of approx. 30 % and an acid rejection of around 15 % depending on the pore size distribution of the specific membrane. The permeability of 80 L/hm²bar could be kept stable over several weeks of operation. Fouling could be controlled by high crossflow velocities of more than 1 m/s. The rejected TOC fraction and thereby the loss of organic carbon in the permeate does not significantly reduce the methane yield.

Currently, a further treatment step with nanofiltration is tested.

Funding:

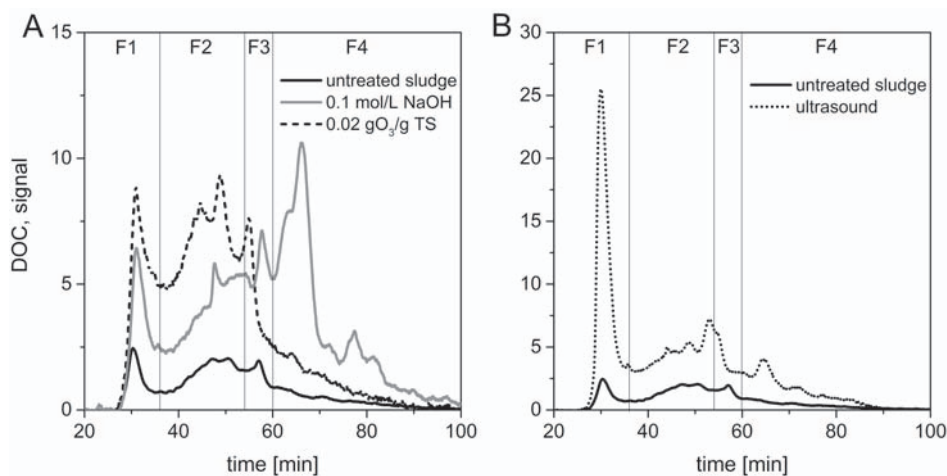
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Universität Hohenheim,
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Universität Mainz, Institute
of Microbiology and Wine
Research, Germany
BIOFAR-EVA, Luxembourg

Energy Saving in Waste Water Treatment Process (ESWaT)

Anaerobic digestion is a proven technique for effective sludge treatment. However, during anaerobic treatment, part of the organic matter in activated sludge is not readily susceptible to biodegradation and conversion into methane. To enhance hydrolysis of organic carbon which boosts methane production, pretreatment of activated sludge is gaining attention. In this project, chemical and mechanical disintegration techniques such as treatment with ozone, sodium hydroxide and ultrasound were applied to enhance sludge solubilization. Biogas production in the digested sludge was monitored to assess the effect of such pre-treatments. To provide more information on the distribution of the released organic carbon after disintegration and its contribution to methane production, size-exclusion chromatography (SEC-OCD) was conducted. The liquid phase of the excess sludge and disintegrated sludge (substrate) were mixed with anaerobic sludge (inoculum) in anaerobic batch reactors and methane production was monitored daily. Samples were collected and analyzed with SEC-OCD. Results show that the different disintegration techniques (0.02 g O₃/g TS, 16 kJ/g TS ultrasound, 0.1 M NaOH) each have different impacts on the quality of dissolved organic carbon (DOC). As can be seen in Figure A, a high amount of the low molecular weight fraction of DOC (60 - 100 min) was released after applying sodium hydroxide, while disintegration with ozone did not change the size distribution of DOC compared to untreated sludge. Additionally, sonication led to an increased abundance of substances with high molecular weights (26 - 36 min) (see Figure B). The effects of these changes on the characteristics of DOC could be observed in methane production. With the same amount of DOC in the anaerobic reactors (100 mg/L), 0.02 g O₃/g TS enhanced methane production by 35 %, while sludge disintegration with sodium hydroxide and ultrasound led to significant increases in methane production of 234 % and 113 %, respectively, compared to untreated sludge. Sodium hydroxide disintegrated the sludge flocs into small molecules and ultrasound released more substances with high molecular weights into the supernatant which could be hydrolyzed easily during anaerobic digestion.



(A) Size distribution of DOC in an anaerobic reactor fed with untreated sludge, 0.1 mol/L NaOH and 0.02 g O₃/g TS. (B) Size distribution of DOC in an anaerobic reactor fed with untreated sludge, and sludge treated with ultrasound.



Elham Fatoorehchi



Stephanie West

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Mekorot, Israel

Beyond Pollutant Removal - Understanding the Biochemical Mechanism of Sulfonamide Degradation in Waste Water and the Role of Ipso-Substitution



Marius Majewsky

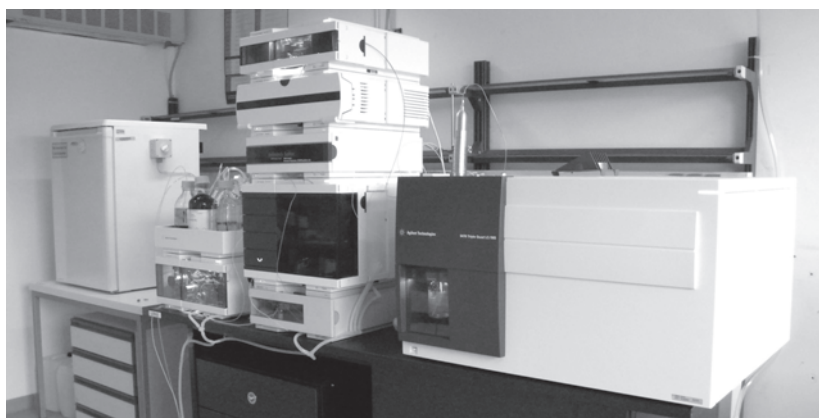
Sulfonamide antibiotics are widely used both for the treatment of humans and livestock. Due to their recalcitrance, they are only insufficiently removed in waste water treatment plants and can therefore be readily detected in effluents, in surface waters and ground water. Constant exposure of microorganisms even to non-inhibitory concentrations has been shown to induce the propagation of antibiotic resistances, which is a cause of concern with regard to the rising number of reports on multi-resistant pathogens.

In the project, we will evaluate whether the identified dead-end metabolites can also be linked to biological sulfonamide degradation. At the same time it will be investigated if the presence of homolog bacterial genes detected in selected waste water treatment plants can be attributed to sulfonamide degrading activity. We will obtain genome sequences from further isolated sulfonamide degrading strains to investigate the presence of *sadA* homologs. From homolog sequences, a consensus sequence will be calculated to serve as a base for polymerase chain reaction (PCR) primers to specifically amplify and quantify *sadA* homologs in activated sludge. Sequences flanking these homologs will be analyzed for the presence of gene clusters resembling that in *Microbacterium* sp. strain BR1. Sulfonamide removal rate of the sludges will be determined by quantification of sulfonamides and dead-end metabolites in influent and effluent of the waste water treatment plants. Additionally, the ability of the sludge to degrade artificially added sulfamethoxazole will be assayed. For pure strains, sulfonamide degradation at various nutrient conditions will be assayed to establish thresholds for up- or down-regulation of genes associated with ipso-substitution of sulfonamides. Our overall aim is to transfer findings from the ongoing project funded by the DFG (in cooperation with the Swiss funding agency SNF) and others to provide a better understanding of sulfonamide degradation in waste water treatment plants, compared to the current practice, which is a mere balance of influent and effluent concentrations of the parent compound, or at best acetylated derivatives of that. Bringing all ends together, it will be possible to assess how much sulfonamides are really degraded, and which contribution to that stems from homologs of the flavin mononucleotide-dependent monooxygenase isolated in the project.

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407 (19), 5707-5717.



The new LC-MS/MS (Agilent 6470).

Advanced Characterization of Refractory Organic Matter in Raw Waters

Most natural organic substances in water are the left-overs of biological activities and products of a huge variety of naturally occurring physical, chemical and biochemical reactions in air, soil and water.

The term humic substances (HS) as the refractory part of natural organic matter (NOM) is often used for an integrative description, and the parameters dissolved organic carbon (DOC) for quantification. Many different approaches have been used to characterize NOM. However, the heterogeneous and high molecular structure of NOM in its manifold appearances makes it impossible to identify the chemical structure in the classical sense. Liquid chromatography, especially size-exclusion (SEC), can be used in combination with online DOC-, UV- and fluorescence detection for a further characterization for the needs of drinking water supply.

The GROM-project aims at the advanced characterization of the changes in the DOC quality during the different treatment steps. In addition, the SEC-UV-OC- and fluorescence method is applied in characterizing the refractory organic matter of different kind of raw waters used for drinking water production (ground water, river water, reservoir water), and during different seasons.

The figures show an example of a reservoir water which was treated by ozone (A) followed by flocculation (B; flocculation with FeCl_3). It is obvious that after the ozonation step there is a slight decrease of the larger molecular size fraction, and a rise of a fraction including small molecular weight organic acids. After flocculation, most of the higher molecular weight organic matter gets eliminated. Especially the high molecular size substances get better eliminated than the small ones.

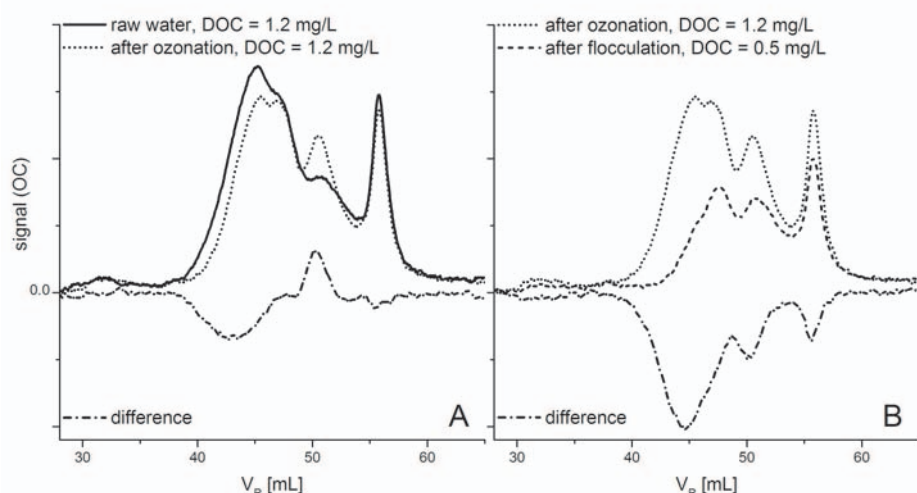
Complementary excitation-emission-matrix (EEM) fluorescence spectroscopy is used as an additional tool for DOC analysis. The fluorescence method is tested in order to compare the applicability of an additional robust alternative for an advanced DOC characterization.



Gudrun Abbt-Braun



Fritz H. Frimmel



OC-chromatograms and the difference chromatogram of reservoir water, A: raw water and after ozonation; B: after ozonation and after flocculation.

Funding:

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Partners:

DVGW Water Technology Center (TZW), Dresden Branch, Germany

Associated in the project TALCO

For further details see:

<http://www.ufz.de/index.php?de=31334>

Do Photocatalytically Generated OH Radicals Originate from Water or Dissolved Oxygen? An Isotope Labeling Study



Aleksandr O. Kondrakov

Fritz H. Frimmel

Illumination of aqueous suspensions of TiO_2 results in formation of electron-hole (e^- - h^+) pairs in the TiO_2 crystals. The h^+ and e^- localized at the TiO_2 surface induce redox reactions with solutes and can be exploited for the water decontamination. h^+ and e^- can react with contaminants via direct electron transfer and/or via $\bullet\text{OH}$ -mediated pathways. Although both of the pathways proceed with similar quantum efficiencies, principally different oxidation mechanisms will occur. The oxidation mediated by $\bullet\text{OH}$ is an unselective, omnipresent reaction, whereas h^+ and e^- react only with adsorbed species. Currently, there is no consensus on the mechanism of the $\bullet\text{OH}$ formation and the fundamental understanding of aqueous TiO_2 photocatalysis is not consistent. Therefore, further investigations on the $\bullet\text{OH}$ formation chemistry are highly important.

This work aimed at the identification of precursors of photocatalytically generated $\bullet\text{OH}$. The identification of the $\bullet\text{OH}$ precursors was performed in isotope-labeling experiments using $^{18}\text{O}_2$ dissolved in H_2^{16}O (see figure). To selectively explore $\bullet\text{OH}$, 1,3,5-trichlorobenzene (TCB) was adsorbed in pores of silica gel (SG) microparticles and the kinetics of its "remote" photocatalytic degradation was monitored. TCB was adsorbed in pores of SG and, by this, was shielded from the direct h^+ oxidation. This allowed to selectively determine the quantum yield of the $\bullet\text{OH}$ generation. The isotope labeling with ^{18}O has demonstrated that the major pathway of the $\bullet\text{OH}$ formation is the direct h^+ oxidation of H_2O , whereas the reduction of dissolved O_2 by e^- contributed in less than 5 % of the total amount of $\bullet\text{OH}$. Nevertheless, the latter pathway becomes more important if h^+ is scavenged. This work sheds light on the intrinsic roles of photogenerated h^+ and e^- in the mechanism of the $\bullet\text{OH}$ formation in aqueous TiO_2 photocatalysis.

Funding:

The Land Baden-Württemberg, ZO IV program

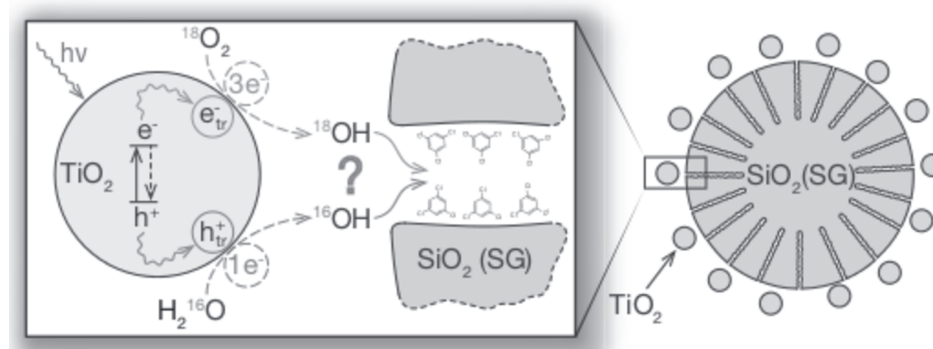
Freundeskreis des Engler-Bunte-Instituts

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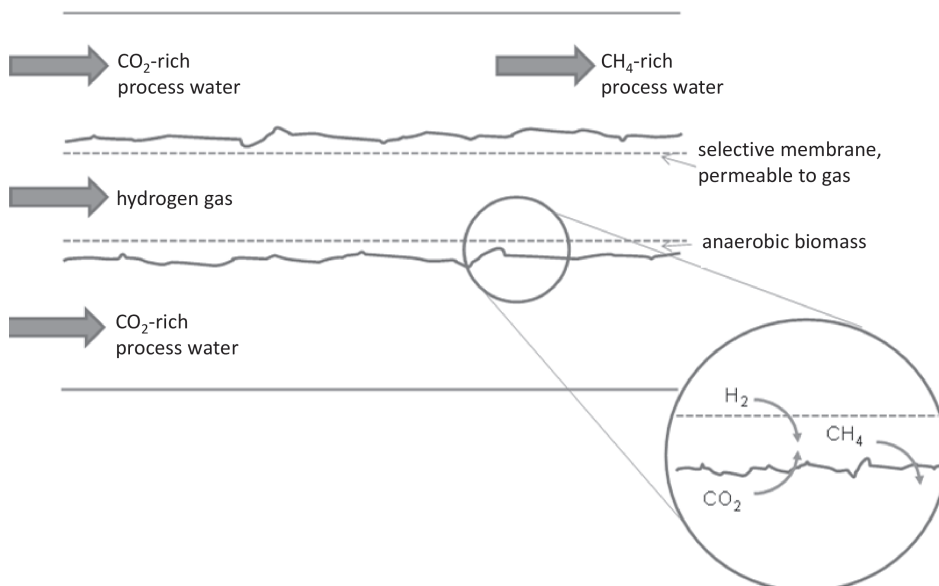
H_2^{16}O and $^{18}\text{O}_2$ as precursors for photocatalytic generation of OH radicals at the TiO_2 surface (left) and a sketch illustrating the "remote" photocatalysis approach using nanoporous silica gel carrier (right).

Productive Biofilms

In waste water treatment, the application of biofilms has been proven to be a successful technology. Lately, many approaches have been made to expand the application to biotechnological processes for the production of both low-cost and valuable complex chemical compounds. The high interest in biofilms is, amongst others, due to a higher space-time yield resulting from higher cell densities compared to planktonic cultures. Other benefits of using immobilized cells for biotechnological production include high system variability and lower susceptibility of the cells to unfavorable growth conditions, allowing for continuous production processes.

The potential of productive biofilms will be investigated in two projects: One project focuses on the different productivities of suspended cells cultivated in batch mode on one hand and biofilm cultivations in a continuous process on the other. The study focuses on product yields, product inhibition and reachable biofilm densities. The formation and structure of mono-species biofilms will also be investigated for different types of substrata, mainly by means of Optical Coherence Tomography (OCT).

The second project deals with the biotic production of methane in anaerobic membrane biofilm reactors. The idea is based on a separation of the liquid and gas phases. The membrane bound biofilm will be exposed to process water rich in carbon dioxide. Hydrogen gas as electron donor will be provided from the other side of the membrane (see figure).



Sketch of the spatial arrangement of biofilm and substrate supply in the membrane biofilm reactors.



Laure Cuny



Isa Remdt



Andrea Hille-Reichel

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Standard Methods for the Examination of Water, Waste Water and Sludge



Birgit C. Gordalla

Funded by the German Water Chemistry Society, the coordination activities to update the German standardized methods for water quality assessment have been continued. This included chairing the meetings of the national technical committee DIN NA 119-01-03 AA "Water examination", and of the ISO committee ISO/TC 147 "Water quality", which met in Philadelphia this year.

About 90 standardization projects were dealt with. Besides revision of already existing standards, half of the current activities go to setting up new ones. Analytes subject to recently initiated standardization projects are hexabromocyclododecane, a flame retardant and pbt substance, and thiourea, which has to be controlled as a waste water ingredient because of its nitrification-inhibiting effect. Perchlorate determination using ion chromatography is being standardized for levels as low as 0.1 µg/L, as these ion affects the thyroid function and is of concern in some groundwaters and pool waters. An attempt is made to quantify organically bound fluorine, chlorine, bromine, iodine or sulfur by combustion ion-chromatography. This method is intended especially for estimate of polyfluorinated compounds (PFC) in water and solid environmental matrices by means of the sum parameter AOF.

Before finally establishing a standard, a validation interlaboratory trial has to demonstrate that the interlaboratory reproducibility of the method is sufficient. At present, such trials are in progress for a subanimal biotest on the estrogenic potential of water and waste water using yeast estrogen screens or in vitro human cell-based reporter gene assays, and for the determination of NSO heterocyclic organic compounds by GC/MS.

The loose-leaf collection "Deutsche Einheitsverfahren zur Wasser- Abwasser- und Schlammuntersuchung", comprising about 300 DIN, DIN EN, DIN EN ISO and DIN ISO standards, is jointly edited by the German Water Chemistry Society and the DIN Standards Committee "Water Practice". Many of these standards are part of the German regulatory framework for waste water.

Funding:

Water Chemistry Society
(Division of the Gesellschaft
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GDCh)



Calibration is the basis for quantification in most water analytical methods. The standard ISO 8466 1:1980 on linear calibration is now under revision.

Water Research Network Baden-Württemberg

Water research in Baden-Württemberg is well advanced and there exists a wide variety of working groups focusing on diverse topics, which are visible at an international level. To take advantage of this potential, the Water Research Network Baden-Württemberg was founded at the initiative of the Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg (Ministry of Science, Research and the Arts of the Land of Baden-Württemberg, MWK). The scope of the Water Research Network is to enhance the collaboration across disciplines and locations in Baden-Württemberg in order to meet the future challenges of water research.

During the establishment phase of the network, an interdisciplinary working group identified future-related topics for water research in Baden-Württemberg and developed an innovative research and structure concept. Based on the suggestions of the working group, the Ministry implemented the new water research funding program of the Land of Baden-Württemberg. As a central component, three interdisciplinary joint projects, so called "Forschernetzwerke" (research networks), will be funded for a period of five years. Each team consists of researchers from natural, engineering and human/social sciences from three universities in Baden-Württemberg, working in an interdisciplinary and transdisciplinary manner. In addition, workshops and conferences will be organized within the network to develop future-oriented research questions to open up longer-term perspectives.

The Water Research Network Baden-Württemberg is coordinated by a board, consisting of the speaker (Harald Horn) and three representatives of universities in Baden-Württemberg. An advisory committee with representatives of all universities in Baden-Württemberg and the Ministry is responsible for the strategic direction of the network. The network is supported by a coordination office, established at the Chair of Water Chemistry and Water Technology (Engler-Bunte-Institut, KIT). The kickoff symposium of the Water Research Network will be held on 14 January 2016 in Stuttgart.



Ulrike Scherer

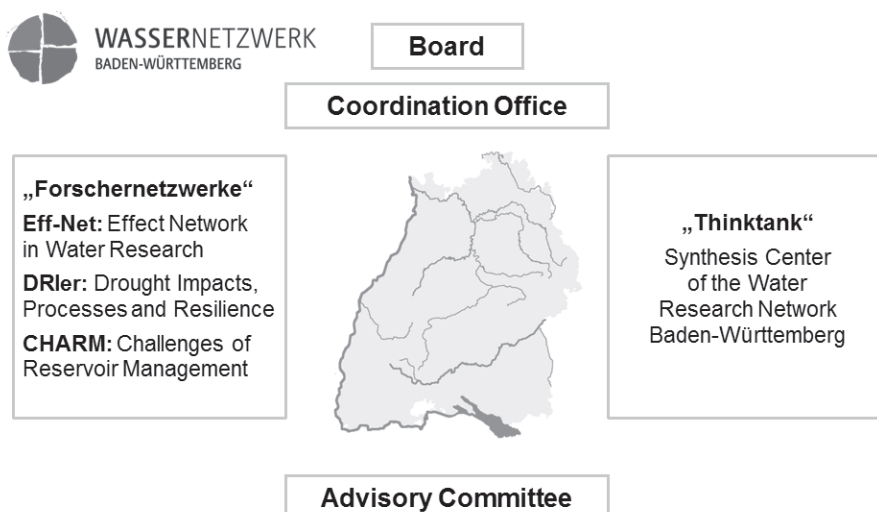


Tanja Stahlberger

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Tübingen, Germany

For further details see:
www.wassernetzwerk-bw.de



Structure of the Water Research Network Baden-Württemberg.

THE WATER CHEMISTRY AND WATER TECHNOLOGY GROUP

Head of Chair

Prof. Dr. Harald Horn
Dr. Gudrun Abbt-Braun

Prof. Dr. Susanne Lackner (since August 2015 at Bauhaus-Universität Weimar)
Prof. Dr. Fritz H. Frimmel (retired)

Supervising Functions and Postdoctoral Positions

Dr. Birgit Gordalla
Dipl.-Ing. Dunja Haak
Dr. Andrea Hille-Reichel
Dr. Marius Majewsky

Standardization, NMR
IT
Biofilm systems
Organic micropollutants

Dr.-Ing. Florencia Saravia
Dr.-Ing. Ulrike Scherer
Dr. Michael Wagner
Dipl.-Ing. (FH) Stephanie West

Membrane technologies
Water Network BW
Imaging
Biofouling

PhD Students

M.Sc. Shelesh Agrawal
M.Sc. Florian Blauert
M.Sc. Dominic Breitkopf
Dipl.-Ing. Fabian Brunner
Dipl.-Ing. Laure Cuny
M.Sc. Elham Fatoorehchi
Dipl.-Ing. Norman Hack
Dipl.-Geoökol. Maria Pia Herrling
Dipl.-Ing. Oliver Jung
M.Sc. Chunyan Li
M.Sc. Di Peng
M.Sc. Jueying Qian
M.Sc. Isa Remdt
M.Sc. Meijie Ren
Dipl.-Ing. Johannes Ruppert
Dipl.-Ing. Marc Tuczinski
M.Eng. Samuel Welker

Microbial population in anammox reactors (since August 2015 at Bauhaus-Universität Weimar)
Biofilms in waste water treatment
Microbial fuel cells in waste water treatment
Aerobic granules for waste water treatment
Productive biofilms
Sludge disintegration and anaerobic treatment
Refractory organic substances in capillary fringes
Fate of magnetic nanoparticles in biological systems
Brackish water desalination
Influence of biofilm structure on reactor performance
Membrane filtration, pool water
Detection of biofouling in irrigation systems
Productive biofilms
Photocatalysis (Dr.-Ing. since June 2015)
Corrosion of piling wall steel (BAW, Karlsruhe)
Membrane technology
Mainstream nitrification/anammox process (since August 2015 at Bauhaus-Universität Weimar)

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(front row) Sylvia Heck, Elham Fatoorehchi,
Sunil Prasad Lohani (guest researcher),
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(fourth row) Harald Horn, Marius Majewsky,
Fabian Brunner, Florian Blauert, Samuel Welker
(last row) Rafael Peschke, Matthias Weber,
Axel Heidt, Oliver Jung, Andrea Hille-Reichel



RECENT PUBLICATIONS

Peer-Reviewed Journal Publications

Blauert, F., Horn, H., Wagner, M., 2015. Time-resolved biofilm deformation measurements using optical coherence tomography. *Biotechnology and Bioengineering* 112 (9), 1893-1905.

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Delay, M., Mangold, S., Sembritzki, R., Frimmel, F.H., 2015. Chromium speciation in solid waste material and eluates by X-ray absorption spectroscopy and ion chromatography. *Aquatic Geochemistry* 21 (2-4), 313-329.

Drosos, M., Ren, M., Frimmel, F.H., 2015. The effect of NOM to TiO₂: interactions and photocatalytic behavior. *Applied Catalysis B: Environmental* 165, 328-334.

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Guthausen, G., Machado, J.R., Luy, B., Baniodeh, A., Powell, A.K., Kramer, S., Ranzinger, F., Herrling, M.P., Lackner, S., Horn, H., 2015. Characterisation and application of ultra-high spin clusters as magnetic resonance relaxation agents. *Dalton Trans* 44 (11), 5032-5040.

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Herrling, M.P., Guthausen, G., Wagner, M., Lackner, S., Horn, H., 2015. Determining the flow regime in a biofilm carrier by means of magnetic resonance imaging. *Biotechnology and Bioengineering* 112 (5), 1023-1032.

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Kondrakov, A.O., Ignatev, A.N., Frimmel, F.H., Bräse, S., Horn, H., Revelsky, A.I., 2014. Formation of genotoxic quinones during bisphenol A degradation by TiO₂ photocatalysis and UV photolysis: a comparative study. *Applied Catalysis B: Environmental* 160-161 (0), 106-114.

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Majewsky, M., Glauner, T., Horn, H., 2015. Systematic suspect screening and identification of sulfonamide antibiotic transformation products in the aquatic environment. *Analytical and Bioanalytical Chemistry* 407 (19), 5707-5717.

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Shen, J., Mkongo, G., Abbt-Braun, G., Ceppi, S.L., Richards, B.S., Schäfer, A.I., 2015. Renewable energy powered membrane technology: fluoride removal in a rural community in northern Tanzania. *Separation and Purification Technology* 149, 349-361.

Books and Book Contributions

Delay, M., 2015. Nanopartikel in aquatischen Systemen. Springer Verlag, ISBN: 978-3-658-08730-2.

Wagner, M., Horn, H., 2015. Biofilme - Eigenschaften, Detektion und Visualisierung. In: Glas, K., Verhülsdonk, M. (Eds.), *Wasser in der Getränkeindustrie*. Fachverlag Hans Carl, Nürnberg, 185-197, ISBN 978-3-418-00817-2.

Publication Series of the Institute

Volume 63: Kondrakov, A.O., 2015. Heterogeneous Photocatalysis and Sensitized Photolysis for Enhanced Degradation of Bisphenol A and its Analogues. 155 p.

Volume 64: Ren, M., 2015. TiO₂: Application in Photocatalysis for the Degradation of Organic Pollutants and Aggregation Behavior in Aquatic Systems. 121 p.

Conferences (Selection)

West, S., Engelke, C., Wagner, M., Horn, H., 2015. Time-resolved visualization and quantification of (bio)fouling in reverse osmosis feedspacer channels using optical coherence tomography, IWA Spec. Conference on Biofilms in Drinking Water Systems. 23.-26. Aug., Arosa, Switzerland.

Abbt-Braun, G., 2015. Behavior of NOM through water treatment processes. XI Encontro Brasileiro de Substancias Humicas (Meeting of the Brazilian IHSS Chapter), 19.-23. Oct., Sao Carlos, Brazil.

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