Karlsruhe Institute of Technology

Topics in Water Chemistry and Water Technology 2019

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

ENGLER-BUNTE-INSTITUT

Dear colleagues and friends,

Another year with extreme weather conditions in Germany and other parts of the world. My favorite biking trail in the Bergpark Wilhelmshöhe was closed off in September this year as the responsible persons in forestry management were afraid that breaking trees could hurt people passing by. Finally, the trees (mainly beeches) were cut down in October.

Climate change is more and more influencing our research topics as the pressure on water resources is increasing both by a higher demand and pollution on the one side and changing processes in surface and in ground water on the other side. Due to a changing water regime and higher temperatures, new contaminants will pop up, which for sure will lead to a need for redirection of our water management in close future.

This year, we have been very successful in collecting research money. You will see the projects on the next pages. In one project, together with BIORESTEC GmbH, the Leibniz Universität Hannover and E&P Anlagenbau GmbH, we will try to recover nitrogen from manure. It took 2 years to finally get funded, which is, with respect to the increasing pressure from the EU on Germany due to nitrate pollution of ground water, a little bit astonishing. We will regularly report on the results within the next years.

Published highlights are for sure the manuscripts of Philip Brown and Oliver Jung. In very nicely designed lab scale experiments, Philip could show that a huge amount of the antibiotic resistance genes (ARG) in river sediments downstream waste water treatment plants are not formed in the sediment but discharged by sewer overflow and suspended solids in treated water. Oliver could, to our knowledge, for the first time measure the concentration polarization above a nanofiltration membrane with Raman microspectroscopy. That is a huge step forward in identification and characterization of scaling and the reward for an extreme difficult calibration process, which had to be done before having the published results.

At the end of this year, we are looking forward to next year, when we will host two conferences:

From June 15 to 17, the Water Research Horizon Conference (http://www.watersciencealliance.org/wrhc/)

and from September 29 to October 1, biofilms 9 (https://www.biofilms9.kit.edu/index.php).

We would be happy to welcome you on one of the conferences.

For 2020, I personally send my best wishes to all of you.

Harald Horn

DVGW

Water Research Network Baden-Württemberg

Ulrike Scherer

Tanja Stahlberger

In 2019, several interdisciplinary workshops took place, covering a broad range of topics in water research. The Universities of Tübingen and Konstanz organized a collaborative workshop on the flash flood in Braunsbach 2016, focusing on how to identify, communicate and tackle risk and vulnerabilities in small catchments. In March, a two-day symposium on risk assessment of substances for the aquatic environment was organized by the team of Effect-Net, one of the three joint projects funded within the framework of the Water Research Network Baden-Württemberg. With more than 110 participants, mainly from research institutes and administration, this event was very well received. Also in March, an open space workshop was held at Karlsruhe University of Applied Sciences on sustainable building of water infrastructures. A collaborative workshop on consistent data bases for hydrological modeling in Baden-Württemberg was initiated by the University of Freiburg in May. Finally, an international workshop on policy approaches to micro-pollutants in water, which was organized by the Institute of Political Sciences of Heidelberg University took place in November.

Another highlight in 2019 was the Black Forest Autumn School on water ages in the hydrological cycle, being held from 27 to 31 October in Freudenstadt. With 6 lecturers and 24 PhD-students from Germany, Switzerland, France, UK, Austria, the Netherlands and Japan, this international school brought together a multidisciplinary experience in the field of measuring and modeling water ages and transit times in environmental systems.

At the beginning of this year, a call for proposals offering start-up funds for the preparation of joint projects in water research was launched. Within this call, three initiatives of the University of Freiburg, the University of Konstanz and the Karlsruhe University of Applied Sciences have been funded.

Upper row: Open space workshop on sustainable building of water infrastructures (left); Black Forest Autumn School (center and right). Bottom row: Participants of the workshop on consistent data bases for hydrological modeling in Baden-Württemberg (left); Panel discussion with PhD students of the Effect-Net-Project and experts from science, administration and industry (right).

Funding:

Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg (MWK)

Partners:

University of Freiburg

Heidelberg University

University of Hohenheim

University of Konstanz

University of Stuttgart

University of Tübingen

Biberach University of Applied Sciences

Furtwangen University

Karlsruhe University of Applied Sciences

HTWG Konstanz – University of Applied Sciences

Offenburg University of Applied Sciences

Stuttgart University of Applied Sciences

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

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

Birgit C. Gordalla

Standardization activities to update the loose-leaf collection 'Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung', which is jointly edited by the German Water Chemistry Society and the DIN Standards Committee 'Water Practice', were continued on national, European and international level. Two methods for assessment of surface waters were relaunched as standards after major revision including a validation interlaboratory trial: semi-quantitative measurement of transparency (DIN EN ISO 7027-2, DEV C 22), and spectrometric determination of chlorophyll-a concentration (DIN 38409-60, DEV H 60). A new edition of DIN 38402-71 (DEV A 71) on equivalence of two analytical methods has been published as a draft, based on a completely revised approach.

The working groups of CEN/TC 230 'Water analysis', developing methods for ecological and morphological assessment of water bodies, held their meeting week in Belgrade. Their host, the Institute for Standardization of Serbia (ISS), became a CEN full member in 2017.

ISO/TC 147 'Water quality', its sub-committees and working groups met in Tokyo, Japan. The meeting was influenced by a typhoon and by lively debates on strategic issues. One of them was the allocation of work on determination of microplastics in water. Pre-normative research in this field has advanced to the stage that the first standardization proposals were submitted. As several ISO/TCs are interested in this topic and duplication of work is not permitted, the projects have to be merged in a reasonable manner. Furthermore, there was a discussion whether commercially available preformatted analytical systems in non-disclosed formats, e.g., sealed-tube tests, can be subject to standardization in ISO/TC 147 and which minimum requirements have to be met with respect to fair competition, disclosure, and comparability. Finally, the experts discussed about non-crucial variability of the single steps of clean-up and enrichment preceding the detection step in mass spectrometry.

Funding:

Water Chemistry Society (Division of the Gesellschaft Deutscher Chemiker e.V., GDCh)

The Umweltbundesamt (UBA)

In October 2019, 95 experts from 20 countries met for the 33rd meeting week of ISO/TC 147 'Water quality' in Tokyo. Several countries, though having delegated experts, were not represented, since about 30 registered participants could not attend. Their flights had been cancelled last-minute due to typhoon Hagibis.

Analysis of Structural and Mechanical Characteristics of Biofilms Using Optical Coherence Tomography

Luisa Gierl

Michael Wagner

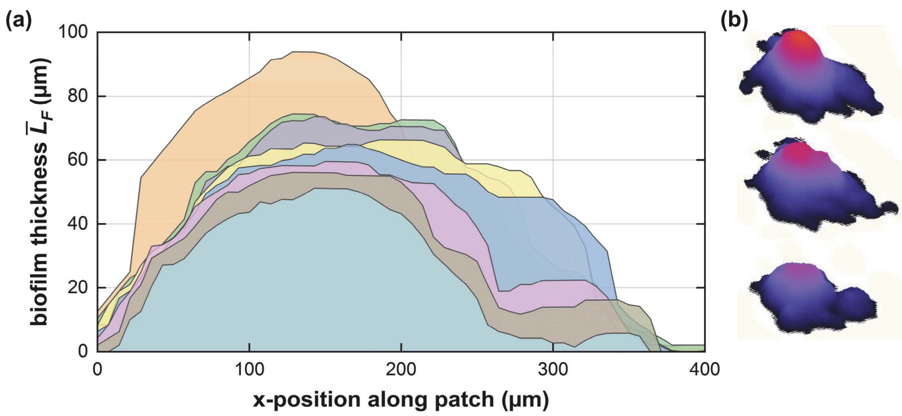
Analysis of biofilm and its properties is an important topic in water research since biofilms are used for the treatment of waste water or provide a habitat for pathogens. Besides many benefits, they can negatively affect industrial settings that are in permanent contact with water, e.g., pipes and other devices, leading to a loss of functionality. To date, biofilm characteristics – as analyzed using imaging techniques – are primarily divided into two parts: structural and mechanical properties. Within the DFG project *Biofilm*, those parameters are analyzed for biofilms growing in minifluidic flow cells while applying different nutrient and hydrodynamic conditions.

As a result, the structural characteristics showed obvious differences when the growth media consisted of 0.25 or 2.5 mg L^{-1} Fe^{2+}, respectively. Biofilms grown under 0.25 mg L^{-1} Fe^{2+} were less developed. They showed a 60 % lower coverage of the flow channel compared to biofilms grown under 2.5 mg L^{-1} Fe^{2+} after 10 days of cultivation. Additionally, biofilm thickness was 15-fold higher for the 2.5 mg L^{-1} Fe^{2+} condition. Under this condition, biofilms also revealed rather flat than steep biofilm aggregates as observed at the lower Fe^{2+} concentration of 0.25 mg L^{-1}. Furthermore, the heterogeneity of aggregates was 3.5 times higher for biofilms grown with 2.5 mg L^{-1} Fe^{2+} and patch sizes changed from day 1 to day 10 by 84 %, whereas at the lower Fe^{2+} concentration of 0.25 mg L^{-1} patch sizes solely changed by 13 %.

Next step within the project is the analysis of Fe^{2+} incorporation into the biofilm and its effect on the mechanical characteristics. Calculation of mechanical properties appeared inconsistent in the past. Thus, different methods are tested to calculate the mechanical moduli in deformation experiments as seen from the illustration below. One approach utilizes optical coherence tomography 3D imaging datasets to extract and quantify information about the deformation behavior.

Funding:
German Research Foundation (DFG)

Partners:
Institute for Computational Mechanics, Technical University of Munich, Germany



Deformation of a single biofilm aggregate/patch under elevated shear stress conditions, illustrated in 2D, back-front (a) as well as in 3D, top-down (b).

BioElectroPlast – Microbial Electrosynthesis for Production of Bioplastics from Flue Gas

Max Hackbarth

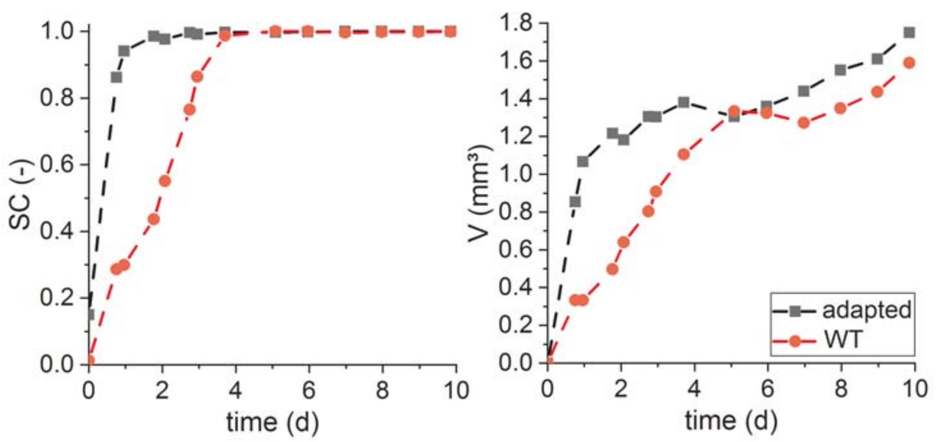
Andrea Hille-Reichel

Michael Wagner

The aim of the project BioElectroPlast is the use of carbon dioxide as feedstock for the production of the biopolymer polyhydroxybutyrate (PHB) in custom-made microbial electrosynthesis (MES) flow-cells. To optimize biofilm growth of the used wild type (WT) of *Kyrpidia spormannii* by means of mutagenesis, initially, the flow-cells were inoculated with a heterotrophically grown pre-culture. For 15 days, biofilm was cultivated on the graphite cathodes, which were poised with a constant potential of -500 mV against standard hydrogen electrode. Afterwards, the grown biofilm was harvested from the cathode and half of it was treated with UV light for 20 seconds. The whole biomass was used as inoculum of a second pre-culture, which then again was introduced into the flow-cells. This procedure was repeated five times.

Subsequently, to investigate the result of the mutagenesis, both, wild type and adapted strain of *Kyrpidia spormannii* were cultivated in the MES flow-cells. Optical coherence tomography 3D datasets were acquired daily for 10 days to monitor biofilm development. The results illustrated in the figure show that the speed at which the cathode is covered with biofilm is almost 4 times higher for the adapted strain in comparison to the WT. Furthermore, also the resulting biofilm volume V is larger throughout the whole cultivation.

These experiments demonstrate that through mutagenesis, *Kyrpidia spormannii* can quickly be adapted to the conditions in the MES flow-cell.



Development of substratum (e.g., cathode) coverage (SC) and biofilm volume (V) of the adapted strain versus the wild type.

Funding:

Federal Ministry of Education and Research (BMBF)

Partners:

Prof. Johannes Gescher, Institute of Applied Biology (IAB), KIT

Center for Environmental Research and Sustainable Technology (UFT), Bremen, Germany

EnBW Energie Baden-Württemberg AG, Germany

Biological Methanation in a Membrane Biofilm Reactor

Andrea Hille-Reichel

Stephanie West

Up to now, a major bottleneck of turnover efficiencies of biological methanation is the low solubility of the substrate gas H_2 in water. As an attempt to overcome this constraint, we investigate the performance of a membrane biofilm reactor, where the substrate gases H_2 and CO_2 are provided via tubular membranes, which are submerged in a flowing aqueous phase. At the same time, the membranes serve as growth substratum for biofilms comprised of methanogenic archaea. In this study, different operation conditions are tested for their applicability and methane production capacities: autotrophic process conditions with a synthetic gas mixture of hydrogen and carbon dioxide to explicitly select for hydrogenotrophic methanogens; autotrophic process conditions with artificial biogas (60 % CH_4 and 40 % CO_2) to test biogas upgrade efficiency; and autotrophic plus heterotrophic process conditions where first, synthetic hydrolysate containing only acetate and second, real hydrolysate from acidic hydrolysis is additionally fed via the aqueous phase to also implement acetoclastic methanation.The figure below depicts the results of a 272 days run in the purely autotrophic mode feeding H_2 and CO_2. Molar flow rates of feed gas are given as F_{in}, flow rates of gas discharged as F_{out}.

The methane production reached a maximum rate of about 1.2 norm $m^3\ d^{-1}\ m^3$ reactor volume, at an almost complete conversion of H_2 and CO_2 from day 235 onwards, when the whole membrane surface was covered with biofilm of sufficient thickness. The gas quality achieved was high, with a methane content well above 90 %. It has to be noted that the reactor configuration was not optimized with regard to the ratio of membrane surface to reactor volume. Based on the methanation rates achieved per membrane surface area, in potential pilot scale reactors, the methanation production can be expected to be significantly higher than the value given here, by a factor of up to 10.

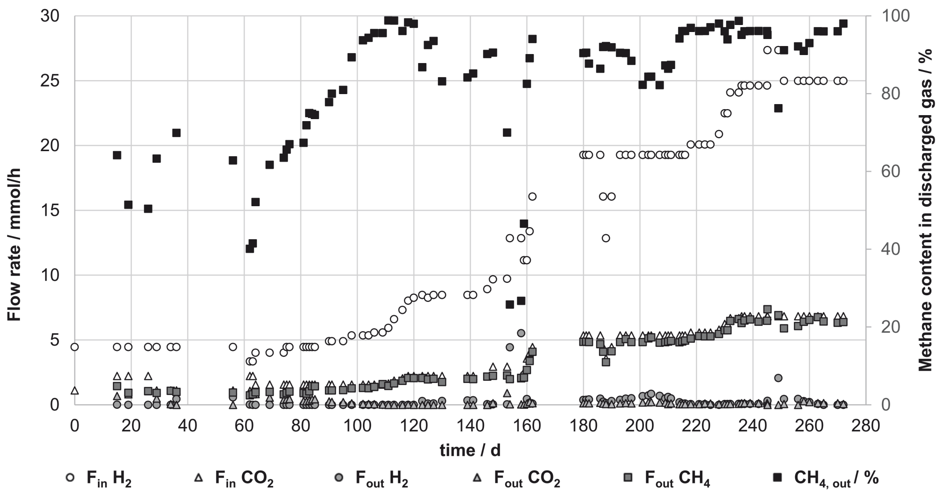
Funding:

Federal Ministry of Food and Agriculture (BMEL)

Partners:

State Institute of Agricultural Engineering and Bioenergy, University of Hohenheim, Germany

Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), Potsdam-Bornim, Germany



Molar flow rates of substrate and product gases in a membrane biofilm reactor.

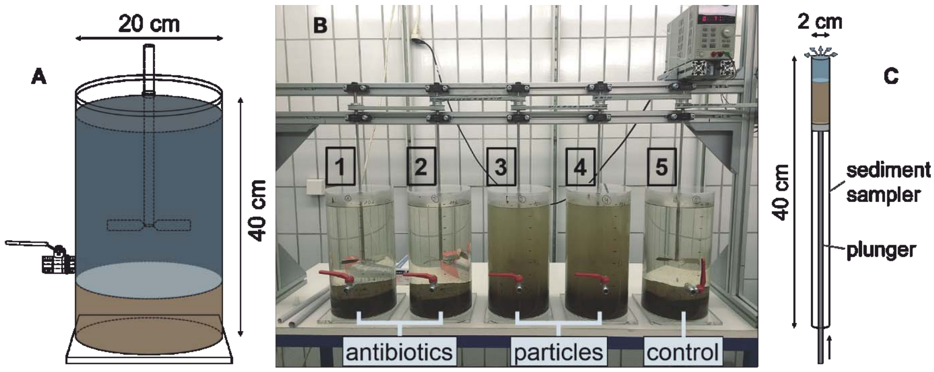
Sedimentation of Waste Water Particles, Associated Bacteria and Antibiotic Resistance Genes

Philip Brown

Ewa Borowska

Large-scale waste water treatment plants (WWTPs) with secondary clarifiers as final treatment step discharge hundreds of tons of particulate matter into surface waters every year. Additionally, a comparable amount is released by sewer overflows during heavy rain events in case of combined sewer systems. Along with sedimentation, particle-attached microorganisms and their antibiotic resistance genes (ARGs) are herewith transported to the riverbed of the receiving water (up to 60 %). To better understand the dynamics of this process, a particulate waste water fraction was added into batch reactors (see Figure), which were previously filled with natural river sediments and tap water. In parallel, antibiotics (ABs) (erythromycin, tetracycline, ciprofloxacin, roxithromycin, penicillin V, and sulfamethoxazole) were spiked to investigate their capability to select for resistance.

The abundance of six ARGs (*ermB, tetM,* bla_{TEM}, *sul1,* $bla_{CTX\text{-}M\text{-}32}$, and *qnrS*) as well as total bacteria (16S rDNA) was monitored in waters and in sediments for a duration of two months using quantitative polymerase chain reaction (PCR). Despite a continuous exposure to ABs (5 µg/L, each), the abundance of ARGs remained unaffected. Addition of waste water particles resulted in a sudden and strong increase of ARGs in waters (3 to 5 log units) and sediments (1 to 4 log units), however, elevated ARG levels underwent a certain and complete decay. Our results indicate that the increased ARG abundances in receiving rivers are the result of a continuous import of ARGs from WWTP discharges or sewer overflow events. They further imply that elevated ARGs do not persist in receiving rivers if this continuous import is removed. For further information, see Brown (2019, doctoral dissertation).



Experimental design. (A) Schematic drawing of one 10 L batch reactor. (B) Photo of experimental setup; taken after spiking waste water particles. (C) Schematic drawing of sediment sampler. According to Brown (2019, doctoral dissertation).

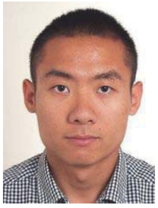
Funding:

German Technical and Scientific Association for Gas and Water (DVGW)

Partners:

Prof. Thomas Schwartz, Institute of Functional Interfaces (IFG), KIT

Reactor Cascades for the Biotechnological Conversion of Waste into Platform Chemicals



Jinpeng Liu

Rowayda Ali

Florencia Saravia

Andrea Hille-Reichel

Michael Wagner

Funding:

Federal Ministry of Education and Research (BMBF)

Islamic Development Bank (IDB) Merit Scholarship Programme, Saudi Arabia

Partners:

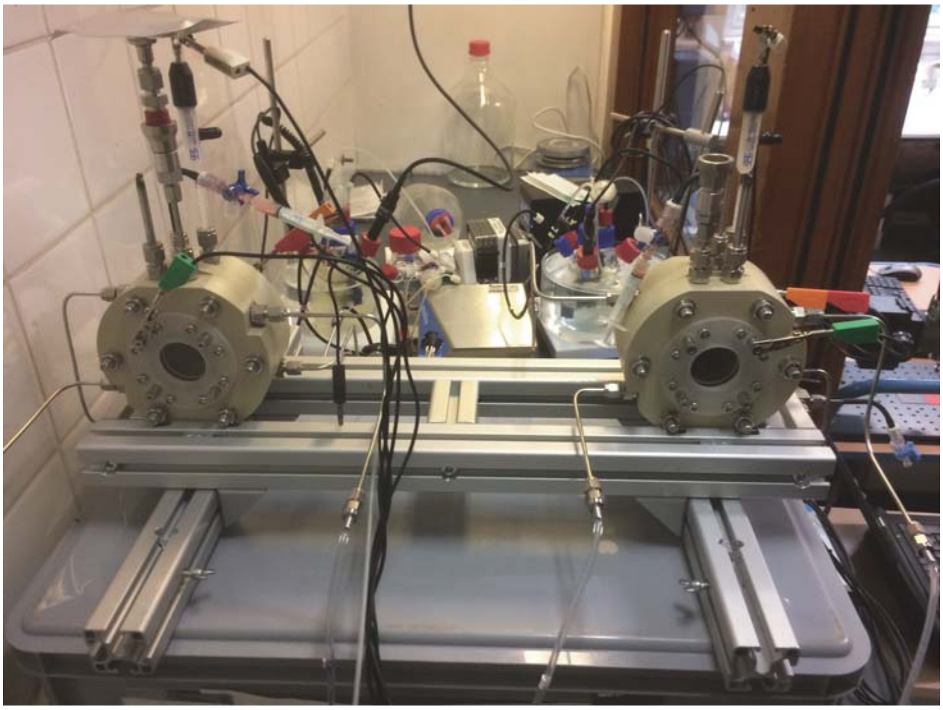
Prof. Johannes Gescher, Institute of Applied Biology (IAB), KIT

Department of Microsystems Engineering (IMTEK), University of Freiburg, Germany

Fraunhofer Institute for Solar Energy Systems (ISE), Germany

The project aims to optimize propionic acid production from organic waste by combining acidic hydrolysis, microbial electrolysis and membrane filtration. In the first step, an anaerobic hydrolysis reactor was operated with vegan dry dogfood as model substrate for organic waste at a pH value of 6.0 ± 0.1 and mesophilic (30 °C) temperature to produce volatile fatty acids (VFAs). In order to optimize the productivity, three different types of inocula were investigated for their suitability in lab-scale batch tests, namely a mixed culture enriched with propionic acid bacteria, pasteurized milk and soft goat cheese. The results showed that the highest propionic acid concentration was achieved with cheese as inoculum yielding approximately 150 and 300 mmol L^{-1} propionic acid in the fermentation of untreated and thermally pretreated dogfood, respectively. Applying this inoculum to the hydrolysis reactor led to a similar maximum concentration of propionic acid of approximately 140 mmol L^{-1} using dogfood.

In the second step of the project, a microbial electrolysis cell (MEC) was contructed to *in situ* characterize and quantify the amount of biofilm by means of optical coherence tomography (OCT) as shown in the Figure below. Three-dimensional OCT images datasets are acquired to assess and correlate electrochemical performance and biofilm growth.



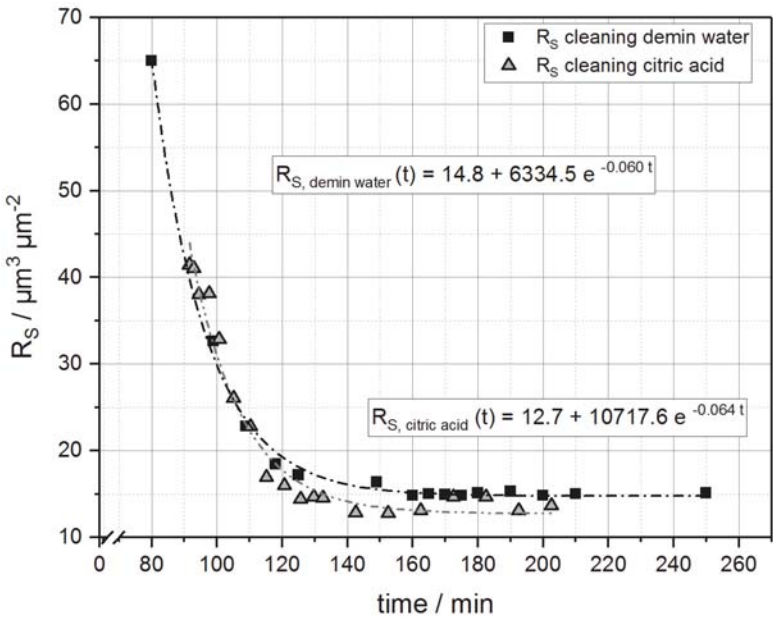
Photograph of MEC system with the special design of OCT window on each side for image acquisition.

Cleaning of Scaled Membranes – A Kinetic Study Based on Optical Coherence Tomography

Membrane distillation (MD) is a promising thermally driven desalination process, operated with a hydrophobic membrane providing a high salt rejection. Fouling, more precise scaling (inorganic deposits), in and on the membrane surface is one of the major challenges in MD operation for desalination purposes. The growth of salt crystals causes a typical flux decline and can result in a considerable deterioration of the rejection properties. Hence, cleaning of the membrane is necessary. Conventional membrane cleaning is carried out after a defined flux decline, following a scheduled standard procedure. An optimized cleaning process – regarding time and quantity of the cleaning agent – can extend the lifetime of the membrane and reduce down times of the desalination plant.

Optical coherence tomography (OCT) was introduced as *in situ* monitoring capable of visualizing inorganic fouling layers combined with an optimized image analysis procedure of 3D OCT datasets. By means of OCT, the kinetics of the scaling removal was described using an exponential function equivalent to $R_S(t) = a + b \cdot e^{k \cdot t}$ as illustrated in the Figure. The exponent k is proportional to the efficiency of the cleaning agent. The calculation of the fouling parameter $R_S = (V_{scaling}/A_{membrane})$ enables the assessment of different cleaning agents, independent of the initial fouling layer amount present on the membrane surface.

Initial experiments revealed, as expected, a similar cleaning efficiency of citric acid (k = -0.064 min^{-1}) compared to demineralized water (k = -0.060 min^{-1}). It is supposed that the slightly increased cleaning efficiency of citric acid is related to its complexation capacity for Ca^{2+}. Further cleaning agents will be tested to draw conclusions on their removal efficiency related to $CaSO_4$. Better cleaning agents should show a k > 0.060 min^{-1}.



R_S values of calcium sulfate cleaning in MD for citric acid and demineralized water as cleaning agents.

Annika Bauer

Florencia Saravia

Michael Wagner

Funding:

Federal Ministry of Education and Research (BMBF)

Partners:

Department of Environmental Process Engineering, Technische Universität Berlin, Germany

DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V., Germany

Fraunhofer Institute for Solar Energy Systems (ISE), Germany

WEHRLE Umwelt GmbH, Germany

SolarSpring GmbH, Germany

Terrawater GmbH, Germany

DEUKUM GmbH, Germany

Increasing Water Availability in Arid Areas: A Method to Assess the Impacts and Adaptability of Different Water Technologies for Sustainable Adaptation

Dámare Araya

Florencia Saravia

Water is transversal to all dimensions of human development and any change in its availability will affect the dynamics of a territory. A comprehensive assessment of the implementation of water technologies is essential to understand the role these technologies play in a territory's development and inform decision-making. This is especially relevant for areas already sensitive to changes in water availability, as is the case of arid areas, where water resources are the main constraint to human growth and where their allocation is an important source of social, environmental and economic conflict.

Understanding that development is a multi-scale and multi-dimension concept and using the Integrative Concept of Sustainability (ICoS) as the overarching theoretical approach to assess sustainability, 23 indicators from more than 2,300 found in literature have been selected and adapted to inform about the impacts of the implementation of sea water desalination and waste water reuse in the development of arid areas.

The scale of the indicators vary from those informing about the technology itself (i.e., energy consumption of the plant), those informing about the direct impacts to the users (i.e., changes in end-user monthly water expenditure), to those revealing the state of important water challenges (i.e., over-allocation of water resources).

As a case study, three scenarios have been developed for the city of Arica, aiming to illustrate the impact desalination and waste water reuse technologies would have in the overall development of the territory. The scenarios are based on 30 variables divided into 5 general topics: urban context, agriculture, economy, health of water bodies and governance.

The next step for this doctoral project is to bring the set of indicators and scenarios to a participative evaluation from stakeholders in the study area, to ensure they are pertinent, relevant and are able to inform decision-making.

Funding:

National Commission for Scientific and Technological Research (CONICYT), Chile

German Academic Exchange Service (DAAD)

Freundeskreis des Engler-Bunte-Instituts

Partners:

Dr. Helmut Lehn, Institute for Technology Assessment and System Analysis (ITAS), KIT

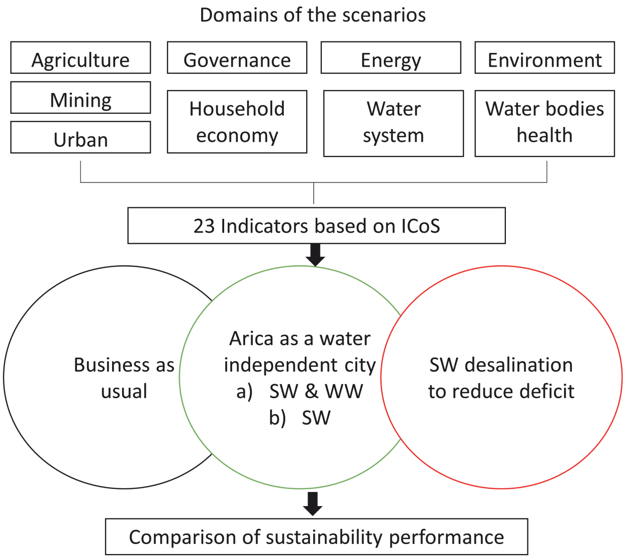


Diagram of sustainability assessment of water technologies in three different scenarios for the city of Arica, Chile (SW: sea water, WW: waste water).

Hydrolysis of Particulate Organic Matter from Municipal Waste Water under Anaerobic Conditions

Particulate organic matter constitutes over 50 % of the organic load entering a waste water treatment plant. From this, 30 to 50 % of the total suspended solids (TSS) reach the biological treatment step. Approximately 30 % of these solids have a particle size larger than 150 µm. According to literature, the size of the particle has an impact on the hydrolysis process: the smaller the particle size, the higher the hydrolysis rate. Hydrolysis is known to be the rate-limiting step in the anaerobic treatment. The formation of the hydrolysis products (HP) and the degradation of the released organic matter can be followed by using the size-exclusion chromatography coupled with an online dissolved organic carbon detection (SEC-OCD).

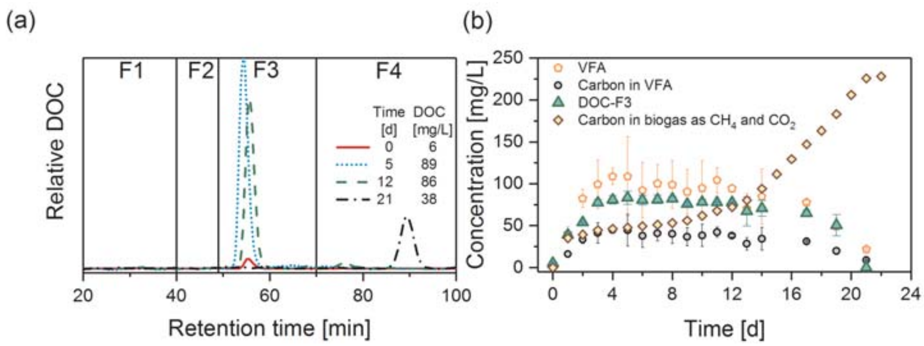
In this work, particles originated from municipal waste water (size: 25 to 250 µm, concentration: 1 g L^{-1} TSS, 0.8 g L^{-1} VSS, volatile suspended solids) were treated under anaerobic conditions in a batch reactor. By using SEC-OCD, the transformation of particles into dissolved matter was studied. The biodegradability of the HP was followed by the determination of the biogas production.

Figure (a) shows chromatograms obtained at the beginning and after 5, 12 and 21 days. The chromatograms are divided into four fractions (F1 to F4), related to decreasing molecular size. In Figure (b), the changes through time of the DOC composition are given. The results show a continuous hydrolysis of particles into dissolved organic matter. Most of the DOC corresponds to fraction F3 (Figure a), which can be assigned to volatile fatty acids (VFA), mainly acetic acid (Figure b). The maximum DOC (DOC in F3 and VFA concentration) is observed on the fifth day, remaining stable until day 12 when the concentration starts to decrease. The methanogenic phase started after 8 days and continued until day 21 when the substrate was depleted (Figure b). Further experiments are conducted to identify the formation and degradation of the HP.

Alondra Alvarado

Stephanie West

Gudrun Abbt-Braun



(a) Size exclusion chromatograms of hydrolyzed chromatographable DOC on day 0, 5, 12 and 21 under anaerobic conditions. (b) Composition of DOC with time.

Funding:

National Council on Science and Technology (CONACYT), Mexico

German Academic Exchange Service (DAAD)

German Technical and Scientific Association for Gas and Water (DVGW)

Fixation of Microplastics from Water Using Organosilanes for Agglomeration Followed by Flotation

Michael Sturm

Within the last decade, plastic pollution has been identified as one of the most relevant environmental problems. Plastic particles smaller than 5 mm are classified as microplastics. They can be directly released into the environment or formed during the fragmentation of larger plastic pieces.

The aim of the project is to use organosilanes to remove microplastics from salt water by an agglomeration process followed by flotation. Fields of application will be e.g., sea salt extraction and desalination.

The applied organosilanes consist of one silicon core atom to which one organic group and three reactive groups are connected. In contact with water and microplastic particles, the organic group attaches to the surface of the microplastics and a so-called sol-gel process starts, which causes the reactive groups bind to each other. This process makes colliding microplastic particles stick together and leads to the formation of large agglomerates, which are chemically bound by the ongoing reaction. As this agglomerates float on the water surface, they can be easily removed.

Laboratory studies showed that additional to the attachment to the microplastics, the organic group has a major impact on the reaction process of the organosilanes in water. Too long or too short organic groups lead to a fast reaction of the organosilanes in water, which avoids an efficient removal process. Intermediate organic groups result in an optimum reaction kinetics, which give enough time for the agglomerate formation and chemically fixes the formed agglomerates in an appropriate time frame.

Currently, the method is tested and optimized on pilot-plant scale for a continuous application.

Funding:
German Federal Environmental Foundation (DBU)
German Federal Ministry for Economic Affairs and Energy (BMWi) through the provision of ZIM

Partners:
Wasser 3.0 / abcr GmbH, Karlsruhe, Germany
Zahnen Technik GmbH, Arzfeld, Germany

Demonstration of the fixation process on pilot-plant scale using polyethylene based microplastics (50 mg/L).

Hybrid Self-Regenerating Electromembrane Process for Removal of Heavy Metals from Water Containing Natural Organic Matter

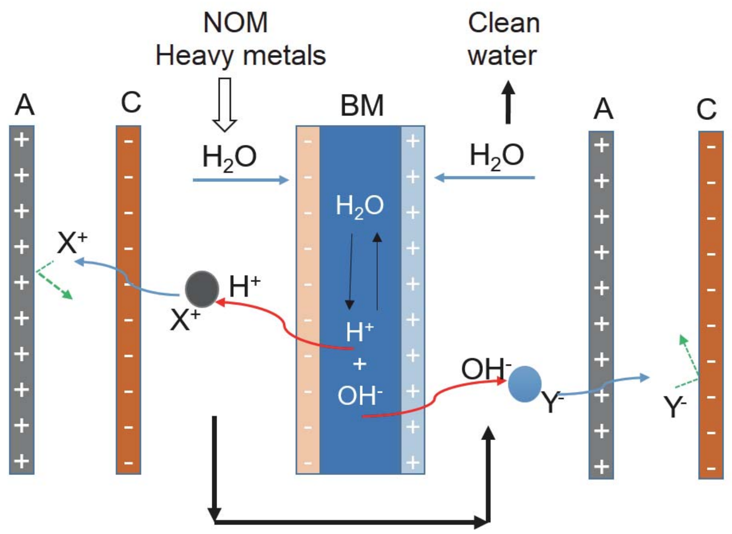
Samuel Bunani
(Guest researcher)

Developing a hybrid electromembrane process offers the possibility to generate a new water purification technology with higher application potentiality worldwide.

The main goal of this project is to produce water free of heavy metals of health concern, and of high concentrations of natural organic matter (NOM) from surface or ground water for drinking water supply or other water applications. This goal should be achieved by using a unique hybrid self-regenerated electrodialysis (ED) process, named ED-IX-BM, that consecutively invests advantages of three processes. The ED-IX-BM laboratory scale system is consisting of a conventional ED stack filled with ion exchange (IX) resins and bipolar membranes (BM).

The hybrid system processed in the ED-IX-BM-stack enables special features such as self-regeneration. By this, ion exchange resins regeneration, and membrane cleaning are overcome. In addition, there is no need of additional chemicals for pH adjustment. Ion exchangers play the role of polishing ED diluate at lower conductivities. The BM is responsible for H^+ and OH^- production. H^+ and OH^- ions are produced from water splitting reaction in the hydrophilic interface of the BM under an applied electrical potential (see Figure). Current efficiencies during ED are maximized by reducing feed water splitting reaction at lower conductivity.

The process is run initially using a model solution containing heavy metals and NOM including common ions of ground water. In the second phase, real ground water samples from contaminated sites will be studied. The efficiency of the ED-IX-BM process is assessed by determining the final water quality, the mass flux of heavy metals and the current efficiency of the process, and the specific energy consumption.



Mechanism of H^+ and OH^- production and ion exchange resins regeneration.

Funding:
Alexander von Humboldt Foundation
Karlsruhe Institute of Technology (KIT)

Effect of Biofilm on Water Retention and Retention Time in Partially Water Saturated Porous Media

Florian Ranzinger

Gisela Guthausen

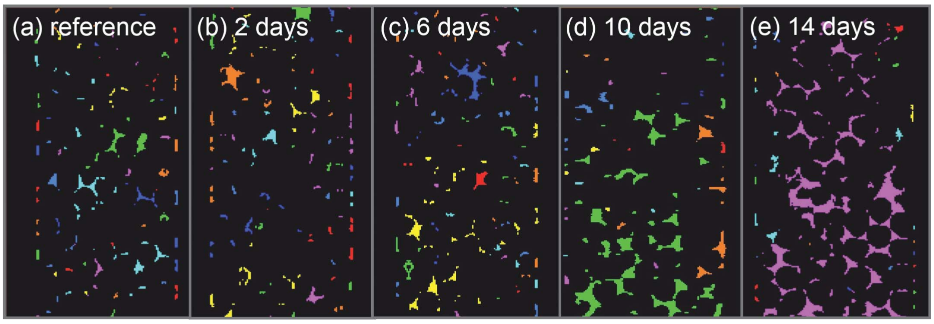
Michael Wagner

Microorganisms settle in diverse partially saturated porous media in form of biofilms. Examples are the vadose zone or biotrickling filters. In these systems, the limited availability of water and its retention time play an important role for the mass transfer to the biofilm and thus for its metabolic activity. The biofilm's extracellular polymeric substances are capable of retaining water against high water potentials. Thus, the aim of the current study was to investigate how biofilm affects the overall water retention as well as the water availability within a porous media.

Magnetic resonance imaging (MRI) was applied for the *in situ* observation of the water content inside the porous media. Prior to the experiments, the biofilms were cultivated under saturated conditions. The model porous media was composed of 2 mm glass spheres. MRI analyses were performed in a 200 MHz NMR tomograph (Bruker Avance 200 SWB) after 2, 6, 10 and 14 days of cultivation. Water retention was determined by monitoring the draining of samples via MRI.

The results indicate that within the first days of cultivation, the water content within the porous media was slightly increasing (see Figure below). Besides water maintained in cavities, the biofilm itself is retaining water. The establishment of a water-retaining network was seen after 10 days of cultivation showing approx. 66 % of water connected within one cluster. After 14 days, 83 % of the detected water was connected, which established a water network through the entire MRI volume (height = 25 mm). Overall, the results indicate that the biofilm increases the availability of water and contributes to a better distribution of water within unsaturated porous media.

Funding:
Karlsruhe Institute of Technology (KIT)



Cross-sectional planes extracted from 3D MRI datasets showing water after draining the porous media. Individual colors represent a liquid cluster (i.e., water volumes that are connected to each other over the 3D dataset). Please note that more liquid clusters than colors are shown. Thus, one color possibly represents more than one liquid cluster.

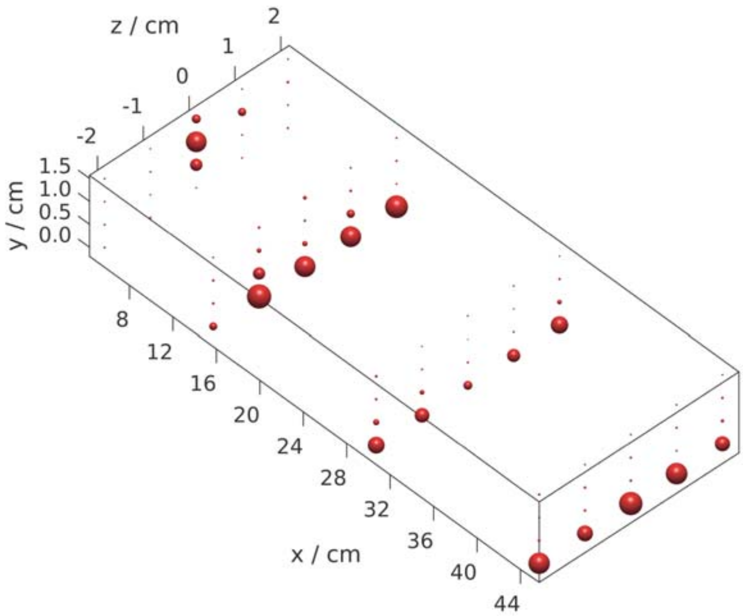
Micro-Organisms and Turbulence: Towards a Numerical Laboratory for Water Quality Prediction – MOAT

Stephanie West

Combined sewer systems collect waste water and storm water runoff. During intense rain events, waste water treatment plants cannot manage the whole waste water (mixed with rain water), which causes a partial discharge of untreated waste water directly into the nearby streams, e.g., rivers. Our objective is thus to understand in more detail the bacteria distribution in rivers after combined sewer overflows.

Experiments were performed in a PVC lab-scale flume with a flow channel length of 1.5 m and a channel width of 10 cm. The water level was adjusted to 1.5 cm. Deionized water was used as bulk phase with a flow velocity of 3.2 cm s^{-1} (laminar). Waste water was spiked as source for bacteria and directly injected below the water surface (≈ 1.5 cm). Samples were collected in a distance of 5, 15, 30 and 45 cm downstream the waste water injection point. To fully resolve the distribution of bacteria in the cross section of the flume, four samples were collected over height (0 cm, 0.55 cm, 1.1 cm and 1.5 cm) and five samples were taken each 1 cm across the width of the flume. In order to achieve quantitative measures for the transport of bacteria, a methodology based on flow cytometry was developed. Briefly, flow cytometry detects and quantifies the size and aggregation of fluorescently marked bacteria. The results are shown in the Figure indicating the distribution of waste water bacteria as total cell counts along the flume.

The size of the red spheres scales with the number of cells found at the corresponding sampling point. Most cells settle within the first 15 cm after the point of injection. Moreover, cells are evenly distributed across the width of the flume.



3D plot over the observed volume within the flume. Red spheres indicate the total cell-counts. (Illustration created by Michael Krayer, Institute for Hydromechanics (IfH), KIT.)

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Partners:
Prof. Markus Uhlmann and Dr. Herlina, Institute for Hydromechanics (IfH), KIT

Fate and Behavior of Antibiotics in River Sediments and their Effect on the Spread of Antibiotic Resistance Genes

Amélie Chabilan

Ewa Borowska

Funding:

Karlsruhe Institute of Technology (KIT)

Antibiotics (ABs) are applied in human and veterinary medicine against bacterial infection and represent one of the most important class of pharmaceuticals. The excessive usage of ABs is often discussed in the context of formation and spread of antibiotic resistance (AR), which is responsible for millions of deaths every year. Despite years of studies, the role of ABs in the dissemination of AR, especially in rivers receiving waste water treatment plants effluents, is not fully understood. Only recently, researchers started focusing on sediments, and still many questions concerning fate of ABs in this environmental compartment remain unanswered.

The aim of the PhD project is to develop a sensitive and robust analytical method for the quantification of a selection of ABs in river sediments and water phase for the concentration range of ng/g and ng/L, respectively. Due to the low ABs concentrations, an elaborated sample preparation including accelerated solvent extraction (for sediments) and solid phase extraction (for sediments and waters) will be adapted for the different AB classes. This developed method will be applied to study the behavior and fate of ABs in a local river, which is impacted by treated waste water. Additionally, in mesocosm experiments, the contribution of individual processes occurring in the river, such as hydrolysis, photolysis, biodegradation and adsorption, will be evaluated, and an effect of ABs on the abundances of antibiotic resistance genes will be assessed.

Processing of Hydrothermal Liquefaction Products with Membrane Technologies

Ali Sayegh

Florencia Saravia

Funding:

European Commission – Horizon 2020

Partners:

Aalborg University, Norway (coordination)

Institute of Catalysis Research and Technology, KIT, Germany

and other partners from Norway, Denmark, the Netherlands, Germany, Spain, Italy and Greece.

Details:

www.nextgenroadfuels.eu

As an attempt to increase renewables in transport energy fuels, the EU launched the *NextGenRoadFuels* project. In this project, biogenic urban resources defined as sewage sludge from treated waste water, food waste and construction wood waste, will be co-processed by our partners in single hydrothermal liquefaction (HTL) facilities. This leads to the production of bio crude oil as well as solid, liquid and gaseous byproducts.

The aqueous phase, produced as a by-product of HTL, is contaminated with several compounds. Ideally, organic compounds should be separated and introduced back into HTL, while inorganic compounds should be recovered before discharge. In addition, separation of the different phases at the product stage of HTL is challenging because of the formation of stable emulsions. Oil-water-solid emulsions shall be processed to recover the oil phase from the water phase.

In this context, our sub-project will study the application of various membrane based processes (e.g., microfiltration, nanofiltration, reverse osmosis, membrane distillation) for the treatment of HTL products. In addition to the measurements of ion retention, retention of organic substances (measured as dissolved organic carbon and single substance analysis), separation of oil from water, membrane permeability and fouling formation will be investigated.

Development and Demonstration of an Energy-Efficient Bio-Electrochemical Waste Water Treatment – DEMO-BioBZ

In 2018 the *BioBZ* project was awarded with the 'Deutscher Nachhaltigkeitspreis'. With the beginning of 2020, we expect the approval of the follow-up project *DEMO-BioBZ*. In case *DEMO-BioBZ* will be granted, the knowledge about bio-electrochemical systems operated with municipal waste water gained during the course of the *BioBZ* project will be transferred to the industrial scale.

In more details, the project aims to (1) design, install and inspect modular replaceable and expandable submers-modules, (2) advanced material development and optimization to minimize cost and material usage for membrane electrode assemblies, (3) development of online control mechanisms for systems employing electroactive microorganisms, (4) optimization of energy harvest, (5) integration of a bio-electrochemical nitrogen elimination into the biochemical fuel cell, (6) conduct of long-term studies, (7) determination and evaluation of performance and design data for COD and nitrogen elimination, (8) determination and evaluation of economic data. These tasks will be solved in an interdisciplinary network of the project partners. We will be involved in working packages related to the optimization of bio-electrochemical setups in order to enhance mass transfer. For this purpose, biofilm visualization and structural characterization by means of optical coherence tomography and image analysis, respectively, will be performed. Results will further be related to macroscopic measures such as produced electrical power, carbon and nitrogen turnover as well as micropollutant elimination.

Michael Wagner

Funding:

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Inst. of Env. and Sust. Chemistry, TU Braunschweig

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Common-Link AG, Karlsruhe

Eurawasser Betriebsführungsges. mbH, Goslar

Umwelttechnik und Anlagenbau GmbH, Plauen

(all from Germany)

Complete Treatment of Manure and Digestate Process Development by Taking into Account Regional Material Flow Concepts for Nutrients and Pollutants

The importance of manure management and treatment in livestock farming and the biogas industry is increasing significantly. In terms of resource management, raw manure and digestate also play an important role in the national nutrient budget. Liquid manure is often applied as an N-rich agricultural fertilizer. However, the chemical characteristics of nitrates make them susceptible to leaching through the soil into ground water. The main obstacles of manure treatment are i) low price range in contrast to the complexity of the process task, ii) strong diversity of asset buyers and operators and iii) uncertainty of the planning situation. The overall objective of the project *KompaGG-N* is to develop a competitive complete treatment of liquid manure and digestate by taking into account regional and industry-specific conditions. The main focus of the partner institute ISAH will be on the sequential evaporation and deammonification process together with BIORESTEC UG and E&P GmbH, whereas we will distinctly focus on optimizing solid/liquid separation by membrane filtration as a pretreatment process for the sequential evaporation and deammonification step. Further identification of the influence of different treatment levels on the retention of micropollutants (especially antibiotics from the animal fattening area) and antibiotic resisting genes will be examined.

Prantik Samanta

Florencia Saravia

Funding:

Federal Ministry of Education and Research (BMBF)

Partners:

BIORESTEC UG, Germany

Institute for Sanitary Engineering and Waste Management (ISAH), Leibniz University Hannover, Germany

E&P Anlagenbau GmbH, Berlin, Germany

THE WATER CHEMISTRY AND WATER TECHNOLOGY GROUP

Head of Chair

Prof. Dr. Harald Horn
Dr. Gudrun Abbt-Braun
Prof. Dr. Fritz H. Frimmel (retired)

Supervising Functions and Postdoctoral Positions

Dr. Ewa Borowska	Organic micropollutants
Apl. Prof. Dr. Gisela Guthausen	NMR/MRI
Dr. Andrea Hille-Reichel	Biological interfaces
Dr.-Ing. Ulrike Scherer	Water Research Network BW
Dr. Michael Wagner	Biofilm structure and function
Dipl.-Ing. (FH) Stephanie West	Head of the laboratory
DVGW Research Center	
Dr. Birgit Gordalla	Standardization
Dr.-Ing. Florencia Saravia	Membrane technologies

PhD Students

M.Sc. Rowayda Ali	Production of platform chemicals
M.Sc. Alondra Alvarado	Characterization of organic carbon in anaerobic and aerobic waste water treatment
M.Sc. Dámare Araya Valenzuela	Decision support for the implementation of water technologies in arid areas
M.Sc. Annika Bauer	Membrane distillation, waste water recycling
M.Sc. Philip Brown	Spread of antibiotic resistance genes in the environment (Dr. rer. nat. since August 2019)
Dipl.-Ing. Fabian Brunner	Aerobic granules for waste water treatment
M.Sc. Amélie Chabilan	Antibiotics in aquatic environment
Dipl.-Ing. Laure Cuny	Productive biofilms
M.Sc. Luisa Gierl	Mechanical and material properties of biofilms
M.Sc. Max Hackbarth	Microbial electrosynthesis
Dipl.-Ing. Oliver Jung	Brackish water desalination
M.Sc. Stephanie Kaschewski	Using smart water data to minimize risk in residential water quality
M.Sc. Oliver Kehl	Influence of aeration in modelling the treatment performance of activated sludge plants
M.Sc. Jinpeng Liu	Membrane filtration
M.Sc. Giorgio Pratofiorito	Concentration of organic acids by means of nanofiltration and reverse osmosis
M.Sc. Florian Ranzinger	Visualization of water and biofilms in porous media
M.Sc. Prantik Samanta	Treatment of manure by membrane processes
M.Sc. Ali Sayegh	Membrane treatment of industrial waste water
Dipl.-Chem. Nico Seeleib	Organic nitrogen detection
M.Sc. Lara Stelmaszyk	PCR- and cultivation-based methods for antibiotic resistence genes
M.Sc. Michael Sturm	Removal of microplastics from sea water
M.Sc. Alexander Timm	Degradation of antibiotics (Dr.-Ing. since July 2019)

Guest Researcher

Dr. Samuel Bunani	Hybrid self-regenerating electromembrane process for removal of heavy metals from water

Technical Staff

Axel Heidt	GC/ECD, GC/MS, AOX
Rafael Peschke	HPLC, LC/MS, IC
Katharina Siegmund	Microbiology, molecular biology
Matthias Weber	LC/OCD, DOC/TOC
DVGW Research Center	
Ulrich Reichert	Operation of lab reactors
Reinhard Sembritzki	ICP-MS, AAS, ICP-OES, IC

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Tobias Grundwald
Kim-Janine Riedle

From left to right:
(first row) Florian Ranzinger, Stephanie West, Samuel Bunani, Sylvia Heck, Ursula Schäfer, Tanja Stahlberger, Florencia Saravia, Matthias Weber, Rafael Peschke, Ewa Borowska, Harald Horn
(second row) Alondra Alvarado, Prantik Samanta, Jinpeng Liu, Axel Heidt
(third row) Michael Wagner, Amélie Chabilan, Luisa Gierl, Rowayda Ali, Birgit Gordalla, Gudrun Abbt-Braun, Ulrike Scherer, Annika Bauer, Reinhard Sembritzki, Ulrich Reichert, Andreas Netsch, Max Hackbarth, Andrea Hille-Reichel, Gisela Guthausen

RECENT PUBLICATIONS

Peer-Reviewed Journal Publications

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Telgmann, L., Horn, H., Schönberger, H., Gescher, J., Abbt-Braun, G., Blöcher, C., Gisselmann, J., Blesgen, A., Wagner, M., West, S., Mann, T., Berger, M., Kern, G., Lemke, J., Klockner, D., Neuber, E., Hebbel, G.W., Werthmann, U., Klinsmann, G., Lawson, J.F., Meyer, H.G., Müller, M., Balser, K., Maier, W., Frieser, J., Thüer, M.; Malaszkiewicz, J., 2019. Wastewater, 2. Aerobic Biological Treatment. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 55 p.

Publication Series of the Institute

Schriftenreihe des Bereichs Wasserchemie und Wassertechnologie und der DVGW-Forschungsstelle am EBI:

Volume 75: Tuczinski, M., 2019. Applikation von keramischen Mikrofiltrationsmembranen in der zweistufigen Biogasproduktion.

Volume 76: Frimmel, F.H., Abbt-Braun, G., Horn, H., 2019. Praktikum Allgemeine Chemie und Chemie in wässrigen Lösungen – Qualitative und quantitative Bestimmungen.

Volume 77: Timm, A., 2019. Einfluss von Sonnenlicht auf den Abbau von Antibiotika in der aquatischen Umwelt: Kinetik, Umwandlung und Wirkung.

Volume 78: Brown, P.C., 2019. Impact of antibiotics and particulate matter from wastewater discharges on the abundance of antibiotic resistance genes in river sediments.

Conferences (Selection)

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