Environmental Technology

Newsletter | Fall 2020

Picture: NASA

Bert Hamelers New Professor at ETE

'Linking electricity to chemistry'

Bert Hamelers, Program Director at Wetsus, has been appointed as a Professor Electrochemical Resource Recovery at ETE. On December 1st, 2020, he will start his new position, which is embedded in the chair Biological Recovery and Reuse Technology, led by Cees Buisman.

'Electrochemistry is a great way to link sustainable energy to chemistry and separation' Hamelers says. 'One of the best-known examples is to produce hydrogen from water by electrolysis.' In this reaction, water is split at the anode into oxygen (O_2), protons (H^+) and electrons. The electrons formed flow through a wire from the anode to the cathode, while the protons in the solution also migrate to the cathode where they are converted with the electrons into hydrogen gas (H_2). Using the same principle, CO_2 can be recovered from air and used as building block in fermentation reactions or in greenhouses to stimulate plant growth.

The ion currents that occur during electrochemical reactions offer many possibilities to recover and separate resources. Typically, positive ions in the solution will move to the cathode, while the negative ones go towards the anode. This principle can be used to remove ammonium (NH_4^+), from urine and manure streams. By using a membrane that only allows the passage of ammonium ions in the solution, they will selectively move to the cathode. Here, ammonium is converted into ammonia gas (NH_3) that can be harvested.

Hamelers is looking forward to the many challenges of his new position, which he will combine with his current activities at Wetus. 'In addition to developing new technologies, my research will also focus on integrating concepts of electrochemistry with running project at ETE', he says. 'But I am also enthusiastic to contribute to education.'

Column

Niels Groot

Water Technology professor at HZ University of Applied Sciences and a water specialist at Dow Benelux

It's an understatement that the chemical industry is facing some challenging decades. Not only the Paris agreement (95% CO_2 reduction by 2050) requires fundamental changes, also the desire to transition towards fossil-free raw materials is a major undertaking. Changes in industry will go along with those in society as a whole, and are thereby subject of public debate and hence politics.

National strategies are being developed, but pathways and combinations are still open (energy sources, storage media, electrification, CCU, plastic recycling, etc.), while in parallel many of the newly required technologies are still at low Technology Readiness Levels (TRL's). Therefore, the risk of less than optimum decisions being taken is high. New technologies are currently being developed, requiring a delicate balance between long term goals and the mid-term target of 50% CO_2 reduction by 2030.

The role of water in this discussion is often overlooked. Although water costs may not significantly contribute to overall investments, the impact of having no water for different processes is tremendous. Also new processes will require heating, cooling or even rely on water as a raw material (like electrolysis for hydrogen production). Climate change will even further stress access to fresh water. Therefore, water experts need a seat at the table.

ETE research continuous despite the Corona virus

Corona has crippled large parts of our society. Especially during the first wave in March and April, many sectors were partially or completely closed down. At Wageningen UR, research activities were reduced, while some labs were even closed altogether. But at ETE, labs remained open and research continued, albeit at a slower pace. Due to a tight planning, good agreements among researchers, and the willingness to stick to the rules, the ETE labs could remain open.

Modutech during Corona times

When the Corona outbreak occurred in early spring 2020, rules and regulations were put in place in the whole country to try to subdue the virus. Society went in a partial lock down and suffered the economic and social consequences. Many Universities shut down their teaching facilities, and went over to online lessons. Many research labs were closed as well and research came to a stop. However, ETE labs remained open and scientists continued their research. 'Closing down our labs would have resulted in disastrous consequences for our research', Operational Manager Vinnie de Wilde says. 'This would have destroyed our bacterial cultures that sometimes took more than year to grow.' Therefore, ETE took a great effort to continue the lab activities, within the limits of the Corona rules. And with success. Now we are in de middle of a second wave, activities still continue.

Continue lab activities

There were some challenges however, to comply with the Corona rules and still keep the labs operational. 'We had to deal with a limited capacity which was determined using the capacity of the air installation in the room in combination with the 1.5-metre distance measure', Laboratory Team Leader, Femke Rambags, says. 'The fact that we have multiple labs, between which people went back and forth, while different numbers of people were allowed in each lab, was an extra complication.' The sample-preparation lab and the instrumental lab were allowed a maximum of seven or three people, while in MODUTECH 10 people could be present at the same time.

Designated work places

To deal with the limited capacity, scientists only performed relatively short activities in labs with a smaller number of people allowed. The tables were divided into designated work spaces, marked with red-white tape on the floor. In addition, researchers were split-up in a morning and an afternoon group. This way, everybody had the opportunity to work daily on their experiments. This required an excellent planning however, and setting priorities in the experimental activities.
To reduce the lab pressure even further, a huge software update that allowed researchers to view and process their analytical data on their own computer, was also realized. De Wilde: 'This update was already planned, but we speeded up its implementation.' Also took a huge step was taken in giving on-line digitalized instructions for new students, regarding instrument operations, lab safety and rules.

Safety culture

Despite all efforts, especially students in the end-phase of their research may suffer delays. This is particularly difficult for those with expiring Visa. However, the university is trying to solve these problems for them. Overall, de Wilde and Rambags are very satisfied how the lab activities are continued in a safe and Corona-proof way, also now a second Corona wave has hit society once more. 'I want to stress that we are able to do this thanks to the efforts of our employees and researchers too', de Wilde says. 'Our safety culture, with many rules and regulation clearly pays off in Corona time. I really appreciate their cooperation and willingness to stick to the rules!'

The sample preparation lab with designated work spaces marked with tape

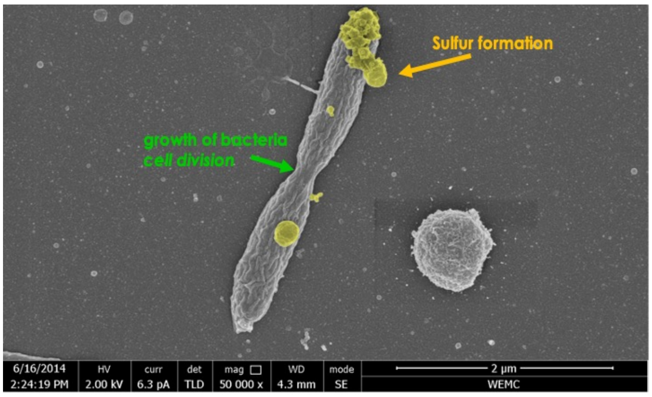
Best Presentation award for PhD researcher Rieks de Rink

During the online ETE congress *Environmental Technology for Impact*, held on June 3rd and 4th 2020, Rieks de Rink won the award for 'best presentation' for his talk *Innovations in Biological Gas Desulfurization*. From over 500 participants and 50 speakers, the majority voted for his presentation, where he discussed new developments and innovations in biological sulfur removal from industrial gases.

'The main aim of my research is to make biological processes to remove hydrogen sulfide (H_2S) from gas more sustainable and efficient', de Rink explains. 'Actually, I presented three innovations and discoveries that help to improve sulfur recovery and reduce chemical, water and energy use.'
The first innovation increased sulfur recovery from gas by preventing H_2S to be converted into sulfuric acid (H_2SO_4). The bacteria responsible for this conversion decreases sulfur formation by competing for H_2S to make H_2SO_4. To increase the efficiency, the H_2SO_4-formation was inhibited in an additional reaction vessel by blocking the bacteria's enzyme systems, responsible for synthesizing H_2SO_4. Under conditions without oxygen, and by elevating levels of H_2S, the scientists managed to knock out most of the H_2SO_4 synthesis. In a second reaction vessel, with oxygen, the sulfur-forming bacteria now have less competition from the H_2SO_4-forming bacteria, resulting in a higher conversion of H_2S into sulfur. The new process also reduces the use of chemicals (NaOH) as well as the waste stream by about 80-90%, which makes the process more sustainable and attractive for use in the oil and gas industry.

The second discovery was that bacteria already play a role in the H_2S absorber, the very first step of the process. In the absorber, an alkaline fluid, like sodium bicarbonate), absorbs H_2S from the gas and converts it into sulfide, HS^-. This HS^--containing fluid is then led into the reactors where the different conversions take place and sulfur is eventually formed. 'We always thought that this absorption step was a purely a physical chemical process', de Rink explains. 'But we found out that the activity of the bacteria already play a role here in the removal of H_2S from the gas stream.'

The third innovation showed that the bacteria taken from the bio-desulfurization process, mainly producing elemental sulfur, can also generate electricity in an electrochemical cell. This offers the possibility to recover energy in the process, making it even more sustainable.

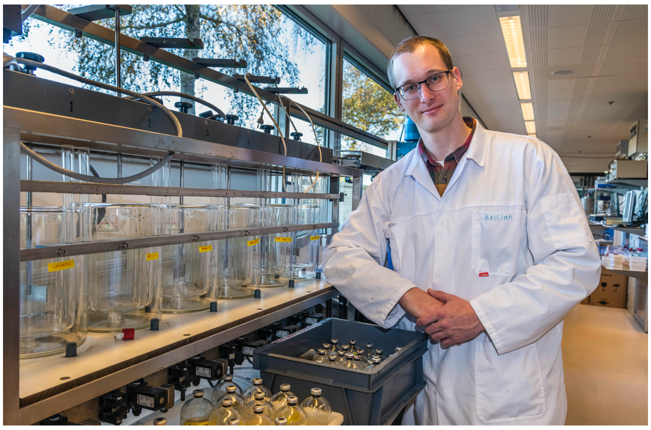


Electron microscopy image of a bacterium oxidizing sulfide to elemental sulfur. The photo shows that the sulfur is excreted and the bacteria is actually dividing.

Science: Converting organic waste into valuable chemicals

Fermentation by microbiota plays a crucial role to recycle organic waste, which is mostly fermented into biogas, a low-grade application. ETE researcher Kasper de Leeuw found a simple, but effective method to stimulate the synthesis of more valuable compounds. By changing the pH, the composition of microbiota present changed dramatically. This resulted in a fermentation that favored the formation of (iso)-butyric acid, an important building block used by the chemical industry. On November 3rd, he successfully defended his PhD thesis: *Open Culture Chain Elongation for Branched Carboxylate Formation*

From waste to value' is an important recycling principle that contributes to a more sustainable society. ETE's research therefore has a strong focus on recovery of energy and chemicals from waste. Often, microorganisms play a key role. For example, to recycle organic waste, microorganisms present break down biomass and convert it into other chemicals. Most often, this fermentation results in the formation of acetate and eventually biogas, or methane. Depending on the different microbiota species present, also more valuable compounds may be formed, such as fatty acids and alcohols. These chemicals have many applications in industry and agriculture as feed additives, solvents, lubricants, bioplastics, fuels etc. Industrial use of these fermentation products is highly sustainable since it reduces the pressure on other resources. For example, many fatty acids originate from fossil oil or palm oil. Especially palm oil production takes a heavy toll on pristine tropical rainforests, that are cleared to make room for oil palm plantations. So, if the right microbiota species are present, fermentation may thus turn organic waste into a resource for high-quality chemicals.



Size matters

The dominant component formed in a 'standard' fermentation is acetate, a short chain fatty acid. In addition, small alcohols, like methanol and ethanol can be formed. In his research, De Leeuw focused on exploring how to manipulate the microbiota species composition to stimulate the formation of high-grade chemicals. During his experiments, he used so-called open-culture bioreactors, that are open to influx of micro-organisms from the surroundings. By manipulating reactor conditions, like temperature, pH, nutrients, and flow rate, he tried to favor microbiota that produce bigger molecules with higher value, like longer-chain fatty acids. With the right microorganisms present, longer-chain fatty acids can be the dominant fermentation products. And for these compounds, size matters: the longer they are, the fattier and oilier their properties and consequently the better their industrial applications. 'For that reason, I tried to select for those species that formed longer, more useful fatty acid molecules', de Leeuw explains. 'I tried to achieve that by, what we call, *chain elongation fermentation,* where a short molecule, like acetate, can be merged with for example methanol, to form a larger reaction product.'

Dramatic shift

Eventually, de Leeuw's discovered that pH was the key to the formation of the desired, bigger molecules (fig. 1): 'A pH change towards either pH 5.2 or pH 6.7 resulted in a dramatic shift in microbiota composition and the products they formed', de Leeuw says. 'At pH 5.2 a *Clostridium* bacteria species dominated, forming a lot of the fatty acid iso-butyric acid. At pH 6.7 an *Eubacterium* was mostly present and formed just butyric acid.' Both compounds have valuable industrial applications. In addition, de Leeuw found small amounts of caproate, another long-chain fatty acid with many possible applications. These microbiota used methanol and acetate to synthesize the longer chemicals. This methanol-based chain elongation required the addition of extra methanol to speed up the process, but according to de Leeuw, that is not a problem: 'Methanol is a simple molecule than can easily be made by certain organic waste fermentations or even from CO_2 gas streams.' So, this process is even more sustainable since it could eventually use a greenhouse gas in the reaction.

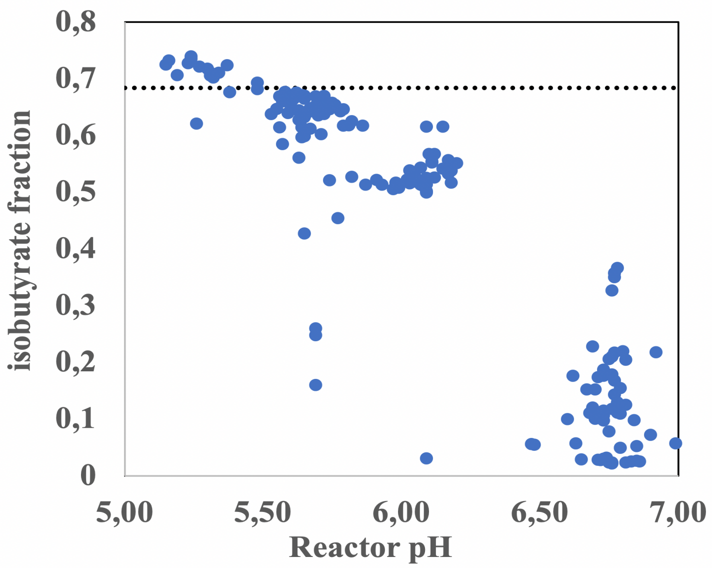


Fig. 1. Isobutyrate formation in an open-culture bio-reactor at different pH values.

Main challenge

De Leeuw's research convincingly showed the proof of principle, with a high reaction efficiency: about 70-90 percent of all carbon present was eventually converted into (iso)butyric acid. The process can now be further tested for the industrial production of these components. According to de Leeuw, the first important test is to make the system work with real organic waste streams in a pilot reactor. The second challenge is to recover the products formed from the watery environment in an efficient and cost-effective way. De Leeuw: 'This down-stream processing is vital for an economically sustainable operation of the process.'

Clogged hoses

Looking back at his four years of research, de Leeuw thinks that perseverance and being attentive were essential. 'Many reactor experiments take months and the main challenge is to have the system operate in a measurements.' These stable conditions were often opposed by clogged hoses, leakages, and failing stable way', he says. 'Only during a steady operation, you can take samples and perform trustworthy equipment. De Leeuw: 'It was crucial to detect those failures early enough to prevent lost time.'

Selected publication

de Leeuw, K., de Smit S.M., van Oossanen, S., Moerland, M.J., Buisman C.J.N., & Strik, D.P.B.T.B. 2020. Methanol-Based Chain Elongation with Acetate to n-Butyrate and Isobutyrate at Varying Selectivities Dependent on pH. ACS Sustainable Chem. Eng. 8, 22: 8184–8194. https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.0c00907

Science: Combining different technologies for cleaning saline wastewater with organic contamination: a step-by-step solution to the problem

Together with project partner Dow Benelux in Terneuzen, ETE researcher Pradip Saha developed a method to clean saline, industrial wastewater. A complex task, since single technologies didn't do the job. Therefore, he combined three different technologies for an effective cleaning: oxidation to remove most organic compounds followed by the use of constructed wetlands to remove some remaining organics. The last step included salt removal by standard membrane desalination technology.

During the manufacturing of chemicals, company Dow Benelux uses substantial amounts of fresh water in their production process. A significant part of their yearly 22 million m^3 fresh water consumption is used for cooling. But in the process this cooling water becomes contaminated. Corrosion and scale inhibitors and biocides are added to prevent scaling and excessive bacterial growth. In addition, due to evaporation, salt concentration increases. The end result is the so-called *cooling tower blow-down water*, that contains a complex mixture of salts and organic compounds. Yearly, around 1 million m^3 of this cooling water is discharged. 'We aim to reduce our fresh water use', Niels Groot (see also column), Water Technology professor at HZ University of Applied Sciences and a water specialist at Dow Benelux, says. 'We don't want to compete for scarce resources.' Therefore, for a more sustainable operation, Dow aims to reduce the use of fresh water by cleaning and reusing the cooling water.

Challenging

However, removing this cocktail of salt and organic substances is challenging. Salt can be removed by by existing membrane technologies, but the organic compounds tend to clog the membranes', Saha says. 'Therefore, we need to remove the organics before desalination.' Since the presence of salt limits microbial degradation of these organic components, Saha had to explore other methods. Previously, Dow explored the possibility to coagulate and subsequently filtrate the wastewater to remove the organics, but this method proved not effective enough.

The application of electrochemical oxidation (EO) was more successful. The principle of this technology is to generate radicals from water by electricity. These radicals consequently degrade the organic substances present. 'By applying current over a cathode and a specially diamond-coated anode, water can be split into a proton (H^+) and a hydroxyl radical ($OH^{\cdot}$)', Saha explains. 'This radical actively degrades the organics, resulting in a 60-70 percent removal. This likely is enough to prevent clogging of the membranes used in the desalination process.'

Major problem

But the successful method proved to have a major problem: the formation of toxic compounds. EO converted the chloride (Cl^-) present in wastewater into the reactive chlorine species. That compound consequently reacted with certain organic substances into highly toxic halide compounds. A first attempt to remove the toxic halide by constructed wetlands was successful, but eventually the plants and bacteria died because halide concentrations were too high. Therefore, the method could not be used and an alternative method had to be found. The scientist went back to the drawing table to find a technology to produce radicals in a completely different way, that avoided the formation of toxic compounds.

Promising

A better option was found in the persulfate oxidation method, a technology that produces sulfate radicals without the formation of toxic compounds. 'By simply adding heat to persulfate, a sulfate radical is formed', Saha explains. 'The heat needed can be extracted from the process, so no additional energy is needed.' The results from Saha's experiments look promising: almost all organics were removed, without the formation of toxic chlorinated by-products. There is however formation of some sulfate in the process.

To add an additional cleaning step where constructed wetlands remove these sulfates, as well as some nitrates, will improve the overall cleaning before desalination.

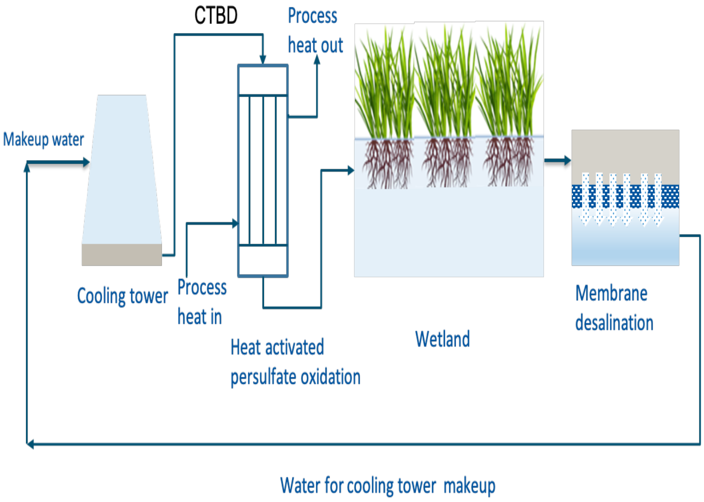


Fig 2. Integrated technology train for cooling tower blowdown (CTBD) treatment

Huge advantage

Despite the success of using sulfate radicals to remove organics, the scientist is now experimenting with UV light as an alternative method to degrade the organic substances. 'For the persulfate oxidation, you need to add sulfate', Pradip says. 'Ideally, you don't want to add any more chemicals.' The first results for the UV oxidation experiments reveal significant organic compound removal, enough to proceed with desalination. However, this method requires the input of extra energy. Project partner Dow really appreciates that the ETE's research has resulted in two attractive options for reusing fresh water, but they have a clear preference. 'In our production, there are quite a few waste streams containing sulfate, and these could be used as a resource for the persulfate oxidation method', Groot says. 'Together with using heat from the process, this is a huge advantage since we can reuse both sulfate waste and heat.'

Selected publication

Saha, P., Wagner, T.V., Ni, J., Langenhoff, A.A.M., Harry Bruning, H. & Rijnaarts H.H.M. 2020. Cooling tower water treatment using a combination of electrochemical oxidation and constructed wetlands. Process Safety and Environmental Protection 144: 42-51.

Agenda

PhD defences (Online):

Paul O'Callaghan, December 9th 2020, 16.00h. The dynamics of water technology innovation.

The defence of Paul's thesis will be the 50th PhD Ceremony of ETE Professor Cees Buisman!

Ilse Voskamp, December 11th 2020, 13.30h. Resource conscious urban planning and design

Laura Piai, February 5th 2021, 13.30h. Micropollutants removal in activated carbon filters: combining adsorption and biodegradation to promote activated carbon bioregeneration

Tania Mubita, February 19th 2021, 11.00h. Selective ion removal in electrochemical processes.

Contact

Annemiek ter Heijne (Environmental Technology)
E: Annemiek.terHeijne@wur.nl
www.wageningenur.nl/ete

Text and pictures by Hans Wolkers (Wild Frontiers B.V.)
E: Hans.Wolkers@gmail.com
www.wildfrontiers.nl, www.science-explained.nl