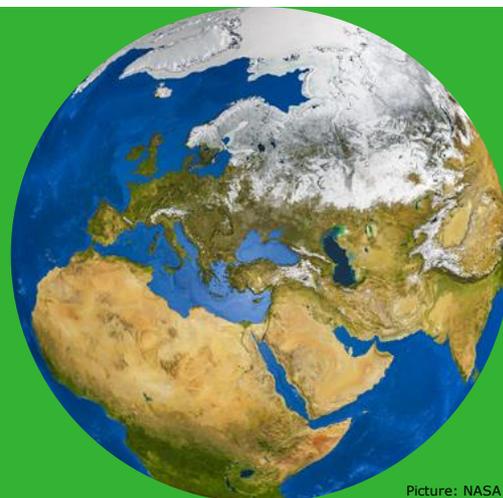


# Environmental Technology

Newsletter | June 2022



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Picture: NASA

## News

### VENI grant for Jouke Dykstra for the electrochemical cleaning of drinking water

With his project on electrochemical 'water polishing', ETE assistant professor Jouke Dykstra has been awarded a VENI grant in the NWO talent scheme Veni, Vidi, Vici. This grant is aimed for excellent scientists that have successfully finished their PhD within the last three years. His project, *Removal of toxic anthropogenic solutes in drinking water treatment by electrochemical polishing*, aims to clean drinking water from low-level contaminants, that are still present after the conventional treatment technologies. The grant offers a personal budget of € 280.00000 for four years of work. Dykstra: 'We will use the grant to develop the technology as well as a simulation model to further fine tune the knowhow and methodology.'



### Innovative technology

To remove the small, harmful compounds that remain after the conventional membrane treatment, Dykstra has proposed an innovative, electrochemical technology that was theoretically validated, together with colleagues from Wetsus and Technion. The system consists of two porous carbon

## Column

Georg Stockinger

**Sr. Water Treatment and Integration Technologist at Shell Global Solutions International B.V., Amsterdam, The Netherlands**

### Creating value from waste streams

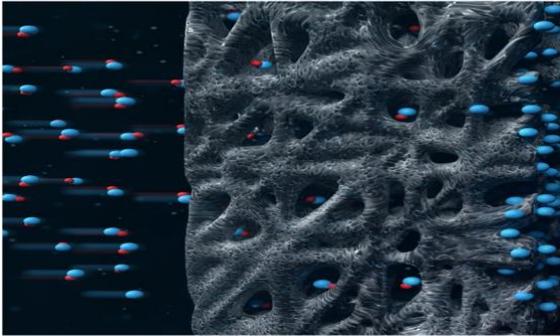
According to the European Parliament, the circular economy is a model of production and consumption, which involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products as long as possible. In this way, the life cycle of products is extended.

On the water-front, one of the "circular" sites Shell operates is the Pearl Gas to Liquids facility in Ras Laffan, Qatar. Here we have learned that, technically, you can recycle on an industrial scale. However, every circular system also produces byproducts. Without these "bleed streams" any contaminant will build-up over time to create a technical and environmental issue, forming a challenge to designing and operating circular systems.

Two of these products are a brine stream from our water recovery systems and biosludge from the biological treatment plant. While these represent only a fraction of the overall mass flow, Shell is trying to reuse these. ETE is helping us investigate the opportunities within the AquaConnect project by evaluating the risks and mitigations of applying industrial biosludge and treated effluent in agriculture, modeling the fate of the different constituents in soil, groundwater and Plant material. Reuse of brine will be investigated further.

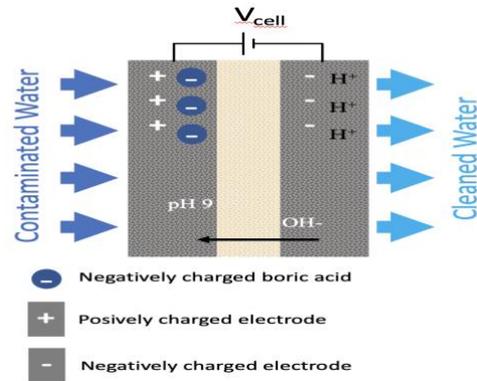


electrodes, where water flows through (Fig. 1). At the downstream electrode, water is split into hydrogen ions ( $H^+$ ) and hydroxyl ions ( $OH^-$ ). The  $OH^-$  migrates to the upstream electrode, increasing the pH. Components, like boron and arsenic act as acids and donate a  $H^+$  in this alkaline environment, and consequently becoming negatively charged. As a result, they adsorb to the negatively charged carbon electrode.



**Impression of the carbon electrode where the contaminants are absorbed. An acid (blue with red balls) enters the high pH electrode and loses a  $H^+$  (red ball). The remaining negatively charged acid (blue ball) sticks to the positively charged electrode.**

'We will use the VENI grant to actually build the set-up and show the proof of principle by removing these contaminants from membrane-cleaned drinking water', Dykstra says. 'Using simulation models, we will also develop and test new electrochemical cell designs and electrode materials for improvement of the technology.' The project will start in autumn 2022 and is scheduled to last until end of 2026.



**Fig. 1. Electrochemical removal of contaminants. Water is split into  $H^+$  and  $OH^-$  on the right-hand electrode.  $OH^-$  migrates to the left side, increasing the pH. Acids, donate a  $H^+$ , and become negatively charged, and are subsequently adsorbed by the positively charged electrode.**

## Science: Cleaning natural gas from toxic components using microorganisms and electricity

**PhD scientists Margo Elzinga developed a safe and clean method to remove the highly toxic thiols from natural gas, using microorganisms and electricity. The proof of principle has been established and the next step is to further understand and scale the process.**

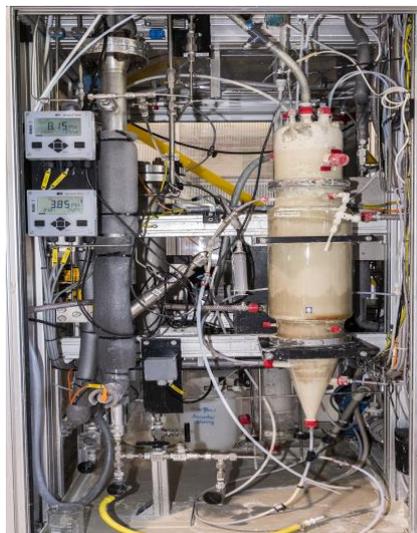
Proudly Margo Elzinga holds a rectangular device consisting of several transparent, plastic compartments that are stacked upon each other and secured with 10 long screws. It looks deceptively simple and only measures about 15 times 7 centimeters. But the chemical reactions that happen inside are rather complex and of crucial importance to Elzinga's research. 'This is my baby', she says jokingly. 'In this bio-electrochemical system the magic happens: here, millions of microorganisms clean the toxic compounds present in natural gas.' The device is divided into two main compartments, separated by a membrane. One compartment is stuffed with porous, black graphite cloth. This is the heart of the device and millions of microorganisms thrive here. Elzinga: 'On

this cloth, microorganisms, with the help of electricity, clean the toxic contaminants present.'



## Polluting procedure

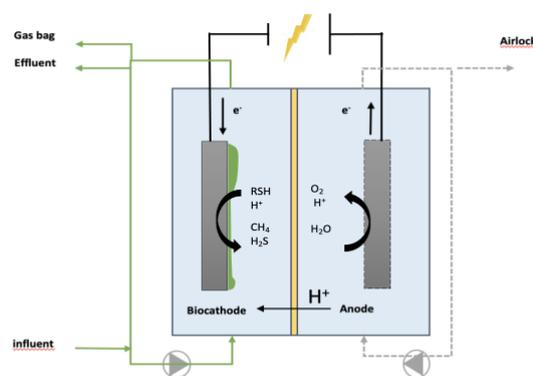
Natural gas contains, among others, the highly toxic so-called thiols or mercaptans, smelly compounds consisting of a carbon skeleton, with a sulfur (SH) group attached. These thiols are just one group of components present in natural gas that need to be removed. In addition, H<sub>2</sub>S is present, but in contrast to the thiols, there is an efficient method for H<sub>2</sub>S removal, and the recovery of pure sulfur, using the famous Thiopaq. This device is a large bioreactor, where microorganisms convert H<sub>2</sub>S into sulfur, following one of the established methods developed by Cees Buisman from ETE in the 1990's. However, the thiols present are not only toxic, they also disturb the elimination of H<sub>2</sub>S, so removal is crucial. 'Currently these thiols are either treated together with H<sub>2</sub>S, lowering the H<sub>2</sub>S removal efficiency, or combusted in which case they'll form sulfur dioxide', Elzinga explains. 'In the paper industry, there is also a thiol problem, that can be solved by bio-filtration, using a biofilter, where microorganisms convert the thiols into sulfate in the presence of oxygen.' However, it is not the best idea to apply this method to natural gas due to explosion danger, while also the volumes to be cleaned in the natural gas are substantially larger. Elzinga therefore developed a new method, where a combination of microorganisms and electricity proved to be highly efficient in thiol removal from natural gas. Her 'baby' plays a crucial part in this thiol cleaning method. Inside the electrochemical system (Fig. 1), two electrodes are present with distinct functions. The anode first splits water into electrons (e<sup>-</sup>) hydrogen (H<sup>+</sup>) and hydroxyl (OH<sup>-</sup>) ions. The H<sup>+</sup> formed moves through a cation exchange membrane, that only allows the passage positively charged ions, to the other electrode, the cathode. Here, microorganisms growing in the graphite cloth use this hydrogen, together with electrons also coming from the anode, and convert thiols into hydrogen sulfide (H<sub>2</sub>S) (Fig. 1). This compound can be further converted into pure sulfur in a next step inside the Thiopaq.



**Sulfur formation in the second reactor vessel of the Thiopaq O&G Ultra pilot plant at ETE.**

## Horrendous smell

When Elzinga started the thiol removal project, there was little knowledge regarding this dangerous group of compounds. 'Nobody knew how to work safely with these dangerous substances, which also has a horrendous sulfury smell', she says. 'I thought it was a really nice challenge, and everybody wanted to help finding a safe way to work with these compounds and remove these compounds from natural gas.' Several years of research later, the new method shows great promise. Although Elzinga established the proof of principle, some challenges remain. For example, she is investigating if the method can be applied to a combination of thiols and not only to the individual ones, she has been testing so far.



**Fig. 1. Schematic overview of the bio-electrochemical system used to remove thiols from natural gas. Water is split into electrons, H<sup>+</sup> and OH<sup>-</sup>. H<sup>+</sup> move from the anode, through the membrane, towards the microorganisms on the cathode. The electrons flow through an external circuit towards the cathode. Thiols (RS) are continuously fed to the cathode, a graphite cloth where microorganisms grow. These convert thiols into methane (CH<sub>4</sub>) and hydrogen sulfide (H<sub>2</sub>S), using the H<sup>+</sup> ions and electrons.**

Also, the stability of the process over longer periods of time is an important factor. Elzinga: 'We have been running the reactor for over a year, and it seems to work fine, although we saw also the formation of other components, like the less toxic diethyl disulfide, thiosulfate and sulfate and we saw traces of elemental sulfur. In fact, this doesn't matter really, it is great too, since also this compound can easily be converted into pure sulfur.' The next step in Elzinga's research is to scale the process and couple the set-up to the Thiopaq, so the system can work as one unit. A kind of a challenge, since the scientist doesn't know for sure which side reactions will take place. For example, how diethyl disulfide will affect the conversion of H<sub>2</sub>S to elemental sulfur in the Thiopaq and vice versa.



It is also not clear how the intermediate products formed in the Thiopaq will affect the thiol removal

system. After four years of research, Elzinga still is enthusiastic about her research on thiol removal. 'It is a real pleasure to work with sulfur compounds, since there are so many different reactions possible, you can really go in all directions, and potentially discover other reactions', she says. 'We still don't really understand in detail what reactions are taking place, but the experiments have clearly shown that our thiol removal method works.'

#### **Selected publication:**

Elzinga M., Dandan L., Klok J.B.M., Roman P., Buisman C.J.N., and Ter Heijne A. 2020. Microbial reduction of organosulfur compounds at cathodes in bioelectrochemical systems. *Environ. Sci. and Ecotechn.* 1, 10009. <https://www.journals.elsevier.com/environmental-science-and-ecotechnology>

## **Science: Reusing treated effluent to combat water shortage: predicting the fate and risk of contaminants**

**Together with Dutch and international partners, PhD researcher Jill Soedarso is studying the safe reuse of effluent for agricultural and nature-related purposes. Her studies are part the project 'Regreening Deserts', within the framework of Aquaconnect. Her project will focus on the behavior and possible risks of contaminant residues, still present in treated effluent. Simulation models will subsequently assess the associated risks.**



Areas facing periods of drought constantly struggle with a stable water supply for agriculture and nature. With a changing climate, these draught periods might increase, resulting in even more water shortage. This poses an even bigger challenge to guarantee a sufficient water supply to the agricultural sector and nature areas. Reusing effluent water is one of the Possible solutions that can be considered to combat

water deficiency. This unexploited water source can be used for irrigation, to enlarge ground water reservoirs, and supplying water to nature, like streams and wetland areas. Not only non-food crop production and desert greening programs can utilize effluent, but also irrigation of food crops is a possibility. However, despite wastewater treatment, effluent may still contain the so-called 'contaminants of emerging concern' (CEC), like pharmaceutical residues and the notorious PFAS. These may pose a risk to crops or human health. Such risks should be understood and quantified to allow for a safe use of such unused water sources.

### **Gas extraction**

Qatar, partner in the project faces a special situation. This country continuously struggles to get enough fresh water. Currently, most fresh water is generated by desalination of sea water, a relatively expensive technology. At the same time, in addition to municipal effluent, Qatar has a lot of waste water available due to gas extraction. This extraction water is treated in wastewater plants, but besides CECs, also large amounts of salts remain after treatment. This poses an additional problem for reuse in, for example, agriculture or desert regreening projects. But despite these problems, the potential of this large effluent reserve is large, especially since the waste water treatment process also results in a large amount of bio-sludge. 'This might be a bonus, since it can possibly be used as a fertilizer on the nutrient-poor soils', Soedarso says.

### **Safe option**

To make effluent water safe for reuse, ETE, together with Dutch and international partners, has started a project to understand CEC behavior in soils and

effluent and possible risks for agriculture. Within the framework of the new Aquaconnect project 'Assessing the fate of contaminants of emerging concern in effluents during irrigation', Soedarso and her colleagues are addressing potential problems and solutions regarding the use of effluent in agriculture. To understand if CECs pose a risk to crops or human health, and if using effluent in agriculture is a safe option, the team aims to better understand how CECs present in effluent behave when used for irrigation. 'We specifically want to find out how, and to what degree, CECs bind to soil and how much end up in the groundwater', Soedarso explains. 'If we understand the interaction between soil, water and CECs, we can develop simulation models to predict the effects of effluent irrigation on soil and groundwater quality, as well as the exposure to crops and humans. This helps us to assess and manage associated risks.' During their research, scientists will establish a link between the Dutch and Qatar casus and develop an overall evaluation for safe effluent reuse.



### Best economical value

As a first step to better understand the fate of CECs in effluent when used for irrigation, Soedarso focuses on experimental studies. 'We will perform experiments to study how CECs bind to soil and how much end up in groundwater', Soedarso explains. 'For example, we aim to quantify to what degree CECs adsorb or chemically react or bind to components in soil.' In the Netherlands, the scientists have planned a series of lab and pilot field experiments, to better understand how CEC bind and migrate through different soils. In Qatar, also experiments are carried out to follow the CECs during their migration through different sandy soil types, using large square soil-filled containers, of 3x3x1 meter in size. By applying effluent on top of the soil, the flow of CECs through the soil, as well as their binding to soil can be followed and quantified. By collecting the water that has percolated through the soil, scientists can evaluate how much of the CECs end up in groundwater. Based on these experiments,

simulation models will be developed, to predict how the CECs may behave in different soils in a real-life situation, and assess the associated exposure risks.



### Experimental site in Qatar

But the study will also include how different crops perform growing on effluent. In addition, water use as well as associated costs and the final crop value will be quantified by Soedarso's project partners. Soedarso: 'Initial experiments conducted last year have shown that cotton does very well. My colleagues in Qatar will experiment with more different crops to see what plant species delivers the best economical value.' In addition, Soedarso's PhD colleague, Alaadin Elozeiri, will develop a good salt removal technology to reduce the high salt concentrations from the gas extraction-related effluent, so this water stream can safely be reused in addition to municipal effluent.

At ETE, experiments will start soon and the initial focus will be on the CEC adsorption to the soil. 'Developing the method is definitely a challenge', Soedarso says. 'The advantage is that we can do these first experiments at a small lab scale, while each test can also be performed rather quickly, within one to two days. That will allow us to experiment a lot of options in a relatively short time!'

### The project "Regreening Deserts" is carried as an international outreach within the framework of Aquaconnect.

**Associated partners are Shell, The University of Qatar, Texas A&M Qatar, Texas A&M, HKUB, Qatar Ministry of Environment and Agriculture. Within AquaConnect, partners related to the Dutch case study are UvA, KWR, Water Agency Vechtstromen.**

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## Agenda

### PhD defences:

Yu Lei, September 23<sup>rd</sup> 2022, 16.00h. Treatment of micropollutants contaminated wastewater effluent by constructed wetlands.

Elackiya Sithampanathan, October 5<sup>th</sup> 2022, 16.00h. A novel solution to remove pollutants from urban wastewater for healthy reuse.

Mariana Rodrigues, October 7<sup>th</sup> 2022, 13.30h (in Leeuwarden). Modelling and application of electrochemical ammonia recovery.

Yujia Luo, October 7<sup>th</sup> 2022, 16.00h (in Leeuwarden). Improving agricultural soil with organic amendments.

Maria van Schaik, October 12<sup>th</sup> 2022, 11.00h. Modelling and optimisation of scenarios for resource recovery from urban sanitation.

Roxani Chatzipanagiotou, November 16<sup>th</sup> 2022, 16.00h. Combining *Chemo*- and *Bio*-Electro- Catalytic Synthesis of Chemicals