Environmental Technology

Newsletter | Fall 2021





News

VIDI grant for biological removal of micropollutants

Nora Sutton, associate professor at ETE, has been awarded a VIDI grant in the NWO talent scheme Veni, Vidi, Vici, for her project on biological removal of micropollutants in groundwater. The VIDI award is offered to young, talented scientists, that got their PhD within the last 8 years. Sutton receives a personal budget of € 800.000. 'Together with cofinancing from drinking water companies, we can spend around a million euros on this project', she says. 'This gives us the possibility to add two PhD students and one postdoc to the team.'



Health hazard

Micropollutants are contaminants, that are present in trace amounts in surface and groundwater sources.

Pharmaceuticals, cosmetics, and pesticide residues are the most common micropollutants in The Netherlands. Groundwater is an important drinking water source, which is usually clean and free of pollutants. However, pesticides originating from agricultural resources, may end-up in some of these water bodies, posing a possible health hazard to consumers. Sutton's project aims to safeguard these water

Column

Sietze van der Velde

Project Engineer at Royal Oosterhof Holman

Phosphate Recovery from animal manure

The Dutch agricultural sector is a global leader. At the same time, the Netherlands face a number of major social challenges. For example, our soil, the most important resource for farmers, is in danger of becoming exhausted. We are also dealing with a loss of biodiversity. This requires a transition towards circular agriculture, in which important nutrients are recovered.

By adding the fundamental knowledge of ETE and Wetsus to the technology and practical knowledge of Oosterhof Holman, we have achieved an important breakthrough, namely the recovery of phosphate from animal manure. This way we can better reuse phosphate and reapply it in agriculture, making us less dependent on the import of phosphate rock. By further developing our innovation and scaling it up to a practical solution for the farmer, we hope to make a valuable contribution to making agriculture more sustainable.

The collaboration between ETE/Wetsus and Oosterhof Holman is about partnership and

Collaboration. In this setting we have built up an excellent team, with also great research results, and hopefully also new products in business for BV The Netherlands!



resources by degrading these contaminants on site in the groundwater, using microorganisms that are naturally present. This is quite a challenge, since microbial activity is low due to anaerobic and nutrientpoor conditions. 'We aim to boost these bacteria's growth by adding growth substrates, like humus, also called dissolved organic carbon (DOC)', Sutton explains. 'But this may pose a risk too, since groundwater is generally clean and contains little bacteria. Adding DOC may result in excessive bacterial growth resulting in a new source of contamination. Therefore, it is a delicate balance to add enough carbon to support the bacteria to degrade micropollutants without adding too much carbon.' Finding and especially understanding this balance to support the biological cleaning procedure is an important part of Sutton's research.

Complex molecules

Another important issue is the choice of the added DOC. Since the micropollutants generally consist of large, complex molecules, Sutton aims to add similarly large and complex DOC molecules, to favor bacteria that are likely able to degrade these pollutants as well. 'During this project, we plan to do both laboratory as well as field experiments to find out which method works best', Sutton says. 'Also, we will model groundwater flows together with bacterial growth under different circumstances.'

Fundamental methodology

The project will provide a fundamental scientific methodology for micropollutant degradation in groundwater that can be applied to other points in the water cycle as well. The project is scheduled to start January 2022 and will last until 2027.

KNCV Crystal growth prize for phosphate recovery from wastewater

Ricardo Cunha, former ETE and Wetsus PhD scientist, was awarded the KNCV Piet Bennema Prize for Crystal Growth 2021 for his thesis 'Anaerobic calcium phosphate bio granulation'. Every three years, the prize is awarded to a young PhD scientist that has published high-level scientific research in the field of crystal growth. 'I was really surprised and honored to receive this award', Cunha says. Cunha's thesis showed scientific depth and a clear practical application to recover phosphate from concentrated wastewater.

Preserve reserves

Phosphate is, among others, present in toilet waste, so called black water. Since phosphate is an essential and

limiting resource, recovery and reuse are crucial to preserve the world's reserves, while reducing pollution. Cunha studied the process of microbial induced calcium phosphate crystal growth during black water treatment using an anaerobic process in a so-called UASB (Upflow Anaerobic Sludge Blanket) reactor. He carried out his experiments at Wetsus with support from DESAH, which operated a demonstration plant in Sneek, where about 200 households are using source-separated sanitation: special toilets, that use much less water for flushing, resulting in a highly concentrated stream (i.e., black water). The black water was collected at the demonstration plant in Sneek and processed in UASB reactors at Wetsus.



Boost crystal formation

By changing reactor conditions, he managed to improve the formation of granules containing calcium phosphate crystals. 'I focused on improving the microbial induced formation of calcium phosphate granules in the sludge bed and their concentration at the bottom of the reactor, where harvesting is easier', he explains. 'Since calcium was not present in sufficient amounts in the black water, I supplied extra to boost crystal formation.' During his experiments, Cunha also noticed that the biofilm that coated the calcium phosphate crystal granules created a slightly higher pH on the inside of the granules. 'The difference was not really large: 7.3 outside and 7.8 inside, on average', Cunha says. 'But the slight increase of pH in the granules enhanced inner crystal growth.'

Sustainable replacement

In addition to enhance the formation of calcium phosphate during anaerobic black water treatment, Cunha also looked into their application as fertilizers. Normally, phosphate rock is used as or to produce fertilizer, and Cunha wanted to see if these recovered granules could be a suitable and more sustainable replacement. 'The granules showed a better phosphate release than powdered apatite, which is found in the traditional Phosphate rock. Also, there were fewer

heavy metals and radioactive materials present', Cunha explains. 'However, a major concern was the presence of pharmaceutical residues in the granules, illustrating the risks of using waste as a resource.' PhD Thesis: **Anaerobic calcium phosphate bio granulation**, 214 pages ISBN 978-94-6343-503-1

Science: Phosphate recovery from animal manure: closing nutrient cycles and improving soil health

ETE PhD scientist Chris Schott managed to efficiently recover phosphate from animal manure by adapting ETE's phosphate recovery technology developed for human toilet waste. The first pilot plant of 5 m³, recovers about 70 percent of phosphorus from animal manure.

Phosphorus (P) is an important and finite natural resource, essential for agriculture as fertilizer. About 70 percent of the natural P reserve that can be used in agriculture is present in phosphate rock in North Western Africa. However, this resource is slowly running out, while P recovery and recycling is at present very limited. In The Netherlands, 71 million kilograms of this nutrient are annually ending up in mainly cow and pig manure. Part of it is reused by farmers to fertilize their crops, but legal limits apply to avoid excess phosphorus to wash out from the soil, harming the environment. As a result, there is a substantial manure surplus, that often is incinerated or transported to other countries, at high economic and environmental costs, since it contains about 90 percent of water. 'Too much P is wasted at high economic and environmental costs, while without this nutrient, we can't grow any crops', Schott says. 'To close nutrient cycles and guarantee food safety, Precovery from manure is essential.'



Coincidentally discovered

The method Schott is using to recover P was coincidentally discovered by PhD student Taina Tervahauta some years ago. She studied ways to increase the efficiency of P recovery from human waste using a traditional anaerobic digestion reactor. In this reactor microorganisms convert organic matter into biogas (methane). She treated separately collected toilet water, also called 'black water', from a demonstration neighborhood in Sneek, equipped with vacuum toilets. After running the reactor for a year, she was surprised to find small granules with a solid core at the bottom of the reactor. The number of granules slowly increased over time from the bottom up and eventually took over the sludge bed. She found similar granules also at the demonstration site in Sneek and realized this might be something new. The scientist started to sample the mysterious granules to determine their composition and found that they mostly consisted of pure calcium phosphate crystals. That was a great find, since these crystals were not only very pure, but could also easily be harvested for reuse because of their size.



Calcium phosphate granules from animal manure

Challenges

Now a new method for P recovery was established, scientists further developed and improved the microbial formation of calcium phosphate crystals from human waste at Water Research Institute Wetsus in Leeuwarden. By adding extra calcium, scientists were able to recover as much as 90 % phosphorus as calcium phosphate granules using the anaerobic digestion reactor. Schott further adapted the method

for P recovery for both pig and cow manure. However, there were several challenges that needed to be met.

In pig manure, the scientists had two main problems. Due to the high amounts of the toxic ammonia present, anaerobic digestion was inhibited, although calcium phosphate granules were still formed. A bigger problem was the high fraction of solids present in pig manure, making it too thick to process. 'These solids mainly consisted of organic material', Schott explains. 'By separating these solids from the nutrient-rich liquid fraction using a screw press (fig. 1), we came a step further, but still reactor pipes were clogging due to many small particles also as a result of adding extra calcium, resulting in more precipitates.' By simply using a bigger reactor with bigger pipes, that problem could be solved, and after adding the extra calcium needed, this resulted in a P recovery of almost 75 percent.

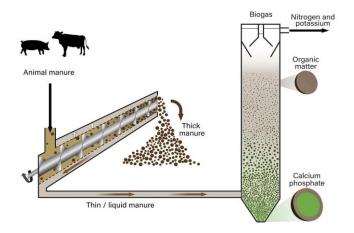


Fig. 1. Animal manure is separated into a thin and thick fraction in a screw press.

Cow manure posed some different problems: after separating the liquid and the solid fractions, there was still a high amount of small fibers present, absorbing a lot of the calcium added, resulting in a lower P recovery and smaller crystals. Still, P removals of 70% were possible, but the recovery, reuse and transportation were more difficult. 'We solved this problem by pretreating the cow manure with a lower pH, that gets rid of some of the fibers present', Schott explain. 'Also, this resulted in overall bigger calcium phosphate granules.'

Improve soil health

The adapted UASB method has resulted in a pilot plant of about 5 m³, that retains about 70 percent of phosphorus present in animal manure, but the scientists believe 90 % is feasible. The whole separation process results in an efficient reuse of organic materials and nutrients: farmers can use the solid organic fraction separated in the first step to improve soil health. The organic matter remaining in

the more liquid fraction is converted into biogas in UASB reactor.

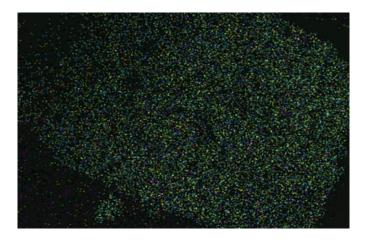


Fig. 2. Energy dispersive x-ray image of a sliced calcium phosphate granule (in green) of about 4 mm.

However, in addition to P, all the nitrogen and potassium are also within this liquid, which allows a separate collection and application of phosphorus from nitrogen and potassium. This can be very useful to dose different amounts of these nutrients but also to fertilize with different timings, since optimal doses and timings differ for crops but also grasses. So, no incineration or transport of raw manure is needed anymore. This approach increases the value of animal manure and stimulates circular agriculture.



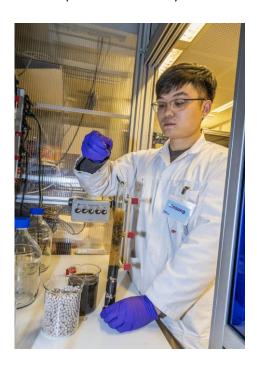
Selected publication:

Cunha J.C., Schott C., van der Weijden R.D., Leala R.H., Zeeman G., and Buisman C.J.N. 2020. Calcium Phosphate granules recovered from black water treatment: A sustainable substitute for mined phosphorous in soil fertilization. Resour., Conserv. and Recy. 158, 104791

Science: Biological degradation of micropollutants using rapid sand filters

By modifying the sand filtration process, used by drinking water companies for water purification, ETE PhD scientists Jinsong Wang improved the removal of the so-called micropollutants. By adapting the operational conditions in the sand filter, like flow rate and available nutrients, he increased the biological degradation of these contaminants. To further develop this drinking water purification method, he is currently focusing on specialized bacteria that are able to efficiently degrade selected micropollutants.

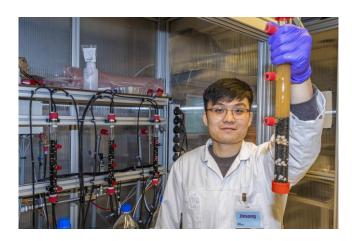
Micropollutants are relatively new, emerging contaminants that include residual medicines, pesticides, and industrial chemicals. These chemicals are difficult to remove from water and this has resulted in more pollutant discharge in drinking water sources during the last decade. Due to improved analytical methods, the presence of these compounds in water has been shown. Many of these micropollutants may cause health effects in humans and animals. For example, they may promote cancer and disrupt the hormonal system.



Increased input

Pharmaceuticals are micropollutants of big concern, but also pesticides used in agriculture may end up in the environment, contaminating rivers and ground water. Today, even pristine ground water sources used for drinking water have already become contaminated with these compounds. In the future, micropollutants are expected to increase in drinking water sources. This inevitably will result in an increased input into produced drinking water. It is therefore crucial to

develop more effective methods for efficient removal of these contaminants from drinking water.



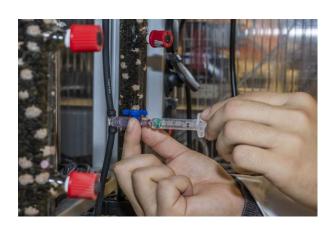
Existing technology

Drinking water companies use microorganisms to biologically clean surface and ground water using, among others, rapid sand filtration. However, these sand filters are rather ineffective to remove some of the micropollutants. As a result, these substances remain in the water and eventually end up at the consumer. To ensure clean and safe drinking water, existing water purification methods need to be improved. Since sand filtration is a commonly used biological cleaning technology at drinking water companies, Wang's research is aimed at adapting this existing technology to enhance micropollutant degradation. This adaptation focuses on modifying the microbial degradation processes inside the sand filtration column. 'We aim to stimulate the growth of specific microorganisms that are capable of degrading micropollutants', Wang explains. 'First, we select different microbial communities and test their abilities to degrade micropollutants. In a next step, we supply different nutrients to boost their growth and subsequently check if there is an increased degradation of micropollutants.' Wang's first experiments showed very promising results: using a simple bottle in his experiments, a so-called 'batch reactor', Wang showed that by adding ammonia and methane, nutrients for nitrifying and methanotrophic bacteria, these microorganisms proliferated and were able to degrade and remove 30-40 percent of the pesticide bentazone present in the test samples, while they almost completely broke down caffeine.

Case-specific operational conditions

To perform his studies in a more realistic way, Wang moved his experiments from a batch reactor, to a column reactor. In this set-up, a continuous flow through a sand bed containing different bacteria, better matched the purification conditions in the sand filtration technology as used by drinking water companies. Wang: 'The main aim of these experiments

was to study how the operational conditions, like flow rate and bacterial food sources, like ammonium and organic carbon concentrations, affected the micropollutant degradation.' The results from the first experiments were somewhat unclear. Adding more nutrients, like organic carbon, resulted in some cases in a better micropollutant removal, for example for paracetamol. However, benzotriazole, a compound used in the chemical industry, showed a lower removal rate by adding more organic carbon. 'I think that the benzotriazole-degrading bacteria prefer just less carbon nutrients for biodegradation, so there is an over-feeding of carbon, resulting in a lower benzotriazole removal', Wang explains. 'That means that depending on the micropollutant present we need to adapt case-specific operational conditions, in this case the amount of nutrients added, for an optimal contaminant removal.'



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Technical optimization

Until recently Wang focused his research on native bacteria, that were naturally present in the sand filter. However, for an even better micropollutant removal, he is currently studying the effect of adding commercially available bacterial strains that are able to degrade specific micropollutants. For example, some strains can degrade the commonly used herbicides 2,4-Dichlorophenoxyacetic acid (2,4-D) and mecoprop (MCPP). Using these commercial strains has some challenges though. 'Since micropollutants are at such low concentrations, the bacteria might not get enough nutrients and consequently die due to starvation', Wang says. 'Also, these bacteria are not as well attached to the sand particles and might be flushed out due to the relatively fast flow rate through the column.' To prevent this, Wang adds extra organic carbon to boost bacterial growth, in addition to porous quartz stones, that shield the bacteria from the flow, so they can grow in a protected environment.' Within a few years, Wang hopes that his research will contribute to using sand filters for a more efficient removal of a variety of different micropollutants for cleaner and safe drinking water.

Selected publication:

Wang, J., de Ridder, D., van der Wal, A., Sutton, N.B., 2021. Harnessing biodegradation potential of rapid sand filtration for organic micropollutant removal from drinking water: a review. Crit. Rev. Environ. Sci. Technol. 51 (18), 2086–2118. https://doi.org/10.1080/10643389.2020.1771888

Agenda

PhD defences (Online):

Joeri Willet, December 10th 2021, 16.00h. From water source to water user: Exploring the potential of alternative water supply sources to supply industrial use.

Jess Wreyford, February 2nd, 2022, 13.30h. Alternative Non-Potable Water Use: Design, complexities, and opportunities.

Andrea Aldas Vargas, February 4th 2022, 16.00h. Biodegradation of pesticides at micropollutant concentrations in groundwater systems

Pradip Saha, February 16th 2022, 16.00h. Biodegradation of pesticides at micropollutant concentrations in groundwater systems

Bignan Song, February $18^{\rm th}$, 2022, 16.00h. Selenium biorecovery (removal) from wastewater to low ppb levels

Annemerel Mol, February 25th, 2022, 13.30h. Crystallization of elemental sulfur in biological gas desulfurization under halo-alkaline conditions.

Merijn Moerland, April 8th, 2022, 11.00h. Thermophilic and hyper-thermophilic anaerobic digestion of concentrated black water for hygienically safe nutrient recovery