wetsus
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WATER CAMPUS
Leeuwarden

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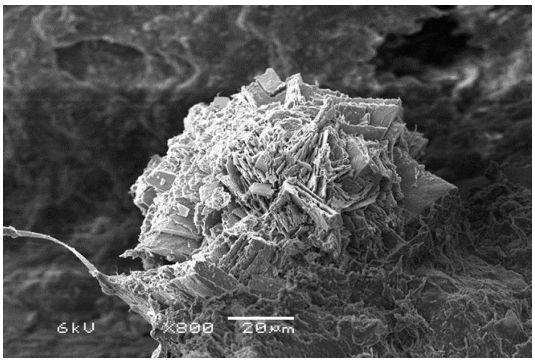
Editorial

Roel Meulepas

Water treatment has the potential to reduce stress on critical resources through the mining of materials and energy from contaminated water streams. The subsequent supply of these Recovered Resources to society will enable circularity. The European Commission accelerates the transition to circularity by investing in cooperative research and innovation projects. These cooperative projects involve top European researchers and innovators that complement each other. Wetsus leads, or participates in such projects, provided they contribute to the Wetsus research programme. Especially the Wetsus research line “Recovered Resources” has benefited from European funding earmarked to support the transition to circularity.
In this S&T Newsletter, four examples of Recovered Resources solutions, investigated and developed through European-funded projects at Wetsus, are presented:

- Researchers in the Phosphate recovery theme explain how the understanding of mineral formation in sewage treatment plants created a novel route for circular phosphate.
- Scientists from the Resource recovery theme combined advances in electrochemistry and membrane science to enable the reuse of the nitrogen, rather than the nutrient being lost to the environment.
- A major breakthrough in the application of Blue energy for wind and solar energy storage is explained by our colleagues from the Blue energy theme.
- And finally, researchers in the Biopolymers from water theme managed to steer microorganisms from sewage sludge to produce biopolymers that form an ideal feedstock for biobased biodegradable plastic production.



ViviMag™ attractive all-purpose phosphate recovery

Using commercial mining equipment, magnetic iron phosphate minerals can be recovered from sewage sludge. These set-ups can be bolted on existing infrastructure, are cheaper, and recover more than current methods can. A must for upcoming legislation while stimulating circular technology and a sustainable environment. The EU project ViviMag™ is a story of microscopic finds to macroscopic application.

Wasted potential

Our society, primarily the European agricultural sector, has depended on imports of the essence of life – phosphorus. Yet it is this pnictogen that has largely been labeled waste. 311 Kilotons phosphorus from untreated sewage flows through the EU’s wastewater treatment systems yearly. That is more than a fifth of the total annually imported phosphate via mineral fertilizer.

Large concentrations of phosphates in surface water have caused algal blooms, making ecosystems suffer. And water quality in Europe in general is strictly regulated. German and Swiss legislation will soon require wastewater treatment plants to recover half of their phosphorus, which is unachievable for most current methods. Though vivianite – a hard-to-detect iron-phosphate mineral – could solve such a problem.

Painting pigment and magnets
The blue mineral has been well known to scientists and documented to be used since at least the Middle Ages. In fact, the great Dutch painters Rembrandt van Rijn and Frans Hals used the pigment in their paintings. Even the Night Watch might contain it.

It is this same mineral that PhD graduate Philipp Wilfert noticed when studying the various phosphate forms in digested sludge. Little interest had been shown in the tiny crystals, yet the Phosphate Recovery team saw great potential.

Part of its unknown presence is because of vivianite is notoriously hard to identify. It takes sophisticated measuring techniques such as X-ray diffraction and Mössbauer spectroscopy to uncover the true forms. And the former method cannot quantify. But Mössbauer can, through its unique fingerprinting. Using a set of gamma-ray energies, the iron containing minerals take up a specific wavelength. This depends on the bond between the metal and surrounding atoms, yielding a spectrum that is solely dependent on iron's neighboring atom.

Details aside, with magnetism as a characteristic, further research was imminent. "ViviMag™ was built on this principle," researcher Wokke Wijdeveld explained, "We started with a small yet powerful electromagnet from the mining industry in the lab, just to show the working principle." The set-up was from scratch, but the materials and infrastructures were well known in other sectors.

It should come as no surprise that the attractive technique saw the potential and interest of various parties. And soon stood a pilot plant in Breda with the help of Oosterhof Holman. Wijdeveld: "This urban mine was a major achievement for the ViviMag™ project. It was far from trivial. Even though the infrastructure was there, there were no instructions to follow. The lab-scale tests were fundamental to the application of vivianite mining and guided us from liter scale to processing a cubic meter per hour."

And with these challenges tackled, the pilot became a success. In a world of possibilities, the scientists saw even more potential. The first tests were with digested streams, yet not all treatment plans have this. So, researcher Thomas Prot investigated the formation of vivianite in other sections of the WWTP.

At first, anaerobic digesters were taken as the main vivianite formation location, but this compartment is not present in all treatment plants. As it turns out, the phosphorus in the form of vivianite reaches all throughout the plant. Sometimes going undetected as causer of scaling. Magnetic retrieval is both circular and an advantage for the treatment systems. As long as there is room for about three days of anaerobic residence time, the blue mineral will form extensively upon iron dosing. "After its biological reduction from Fe-III to Fe-II," Prot explains. "And it will require more iron dosing. The first parts you put in will be consumed through iron sulfide precipitation. Ferrous affinity for sulfides is much higher than for phosphates." So still, minor adjustments for major effects.

A fruitful vivianite future
The result is a near-universal urban mining set-up that can recover up to 60% of all phosphorus entering the treatment plant, program coordinator Leon Korving says. "With that, this method is at least two times more effective than current state-of-the-art struvite recovery. Which even requires particular infrastructure. There is a way to regain more phosphate from ash after sludge incineration, but transportation and even more specialized infrastructure are needed." So vivianite is a very good bet.

Wijdeveld: "With vivianite extraction from the sludge, the plants can dispose their sludge for cheaper as it contains less phosphate." Plus, phosphate itself can be an income. The theme will also focus on extracting the element from manure, as it is a four times larger source than treated water. And vivianite has potential as a stable sink mineral in lakes to combat eutrophication. More research will follow.

Moreover, a fruitful future is expected – vivianite fertilizer tests are said to be done this summer. They seem to be the perfect growing supplement to crops requiring iron and phosphate, such as strawberries.

But for now, the process is being commercialized by Kemira and further upscaling tests are planned in the near future in three European countries. A true display of its success.

ViviMag™ and the phosphorus theme are a collaboration of:

Kemira, Brabantse Delta, Waterbedrijf Limburg, VandCenterSyd, Aquaminerals, Royal HaskoningDHV, TU Delft, Wetsus, and former partners STOWA and ICL

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

Who is Kemira?

"*Kemira is a global leader in sustainable chemical solutions for water intensive industries. Kemira provides best suited products and expertise to improve customers' product quality, process and resource efficiency. Kemira's focus is on pulp & paper, water treatment and energy industry. In 2021, Kemira had annual revenue of around EUR 2.7 billion and around 5,000 employees.*

Read more:

Wilfert, P., Dugulan, A. I., Goubitz, K., Korving, L., Witkamp, G. J., & Van Loosdrecht, M. C. M. (2018). Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. *Water research*, *144*, 312-321.

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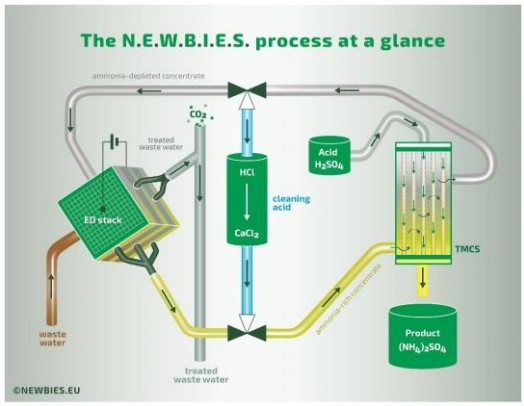
NEWBIES

Shortcutting the nitrogen cycle



Urban mining is the future. Heaps of reactive nitrogen in the form of ammonia, nitrate, and nitrite are processed in wastewater treatment plants. They end up in the atmosphere as N_2 gas, to be consequently fixated again as reactive nitrogen. LIFE-NEWBIES showed that we could shortcut this cycle. With urine and other "waste" streams as the undervalued and untapped resources, this EU Life project built a pilot that processes 1-2 cubic meters of wastewater a day, recovering up to a kilogram of ammonium.

Our relationship with nitrogen

One to two percent of the world's energy is used to generate fertilizer from thin air – the Haber-Bosch process that fixes inert nitrogen gas into reactive ammonia is very energy-intensive. But, we cannot go without nitrogen fertilizer. Nitrogen is essential element for life, being incorporated all throughout every living cell. On the other hand, nitrogen can be seen as malignant. It forms a very potent greenhouse gas N_2O – being 300 times more potent than CO_2.

Yet, these two are linked. What was made into ammonia-fertilizer often ends up in waste streams to be converted into N_2 again, costing energy at both ends. It is a waste of resources not to exploit these nitrogen-rich streams. Wetsus' resource recovery team already noticed this a decade ago within the Value from Urine project, in which the basis of the LIFE-NEWBIES technology was developed. Now, its successor has shown progress in both treatment efficiency and capacity.

An untapped resource

"We have a long way to go in accepting that our *waste* is in fact, an untapped resource," says scientific project manager Philipp Kuntke. "There is plenty of untapped ammonia-nitrogen around, but we see it as waste." The technology to access these reserves is already here, in the form of the NEWBIES pilot plant.

Kuntke focused during his PhD research on (bio)electrochemistry to recover ammonia from urine. The results were so exciting that he continues on this path to this day.

It started with small lab-scale set-ups with 100 cm^2 membrane area and ammonia removal from simple wastewater as a proof of concept. Over the course of the project these molecular sieves grew several hundred times (3.15 m^2) in the membrane area and can now process a thousand-fold of the nitrogen-containing *wastewater* streams.

Not without troubles, though. The highly complex nature of such a refinery meant that every fundamental detail needed to be figured out. Significant challenges that had to be overcome include the system design and the troubles, e.g. inorganic scaling.

Firstly, the choice of membranes to use had to be worked out. An up-scaling using state of the art bipolar membranes (BPMs) and cation exchange membranes (CEMs) seemed the way to go. By stacking CEM and BPM in pairs and thereby defining the diluate and concentrate compartments a compact and effective design was obtained. At the lab-scale, this innovative configuration allowed to retrieve up to 80% ammonia supplied to the system at an energy demand of 18 kJ/gN. The Haber-Bosch Process uses approximately 37 kJ/gN, which shows that electrochemical ammonia recovery can be an exciting pathway.

During prolonged operational periods, scaling became an issue – increasing electric resistance and energy use. Researcher Mariana Rodrigues sought after a chemical-free solution to combat this. Using Donnan dialysis, the team increased the operational window of the NEWBIES technology before calcite deposition hampered the operation.

This system could then be tested with more than just simple wastewater. Digestate, urine, and waste leachate were all run through the LIFE-NEWBIES Pilot installation. And though the energetic demand increased, the team successfully managed to produce fertilizer from these streams.

Rodrigues showed the effectiveness of recovered ammonia. She managed to grow spinach and radish in the laboratory. The electrochemical recovered ammonium nitrate and sulfate were shown to be a viable alternative to current commercial fertilizer but are not yet allowed due to current legislation.

A fertile future

Although concerns about contamination from waste sources are legitimate, these risks can be averted with technological advancements. Kuntke: “Next to a proper and effective treatment system, in the end also public acceptance of the fertilizer and compliance to legislation are of great importance for the future development of the technology.” All *urban and waste mining* concepts need to demonstrate the safety, effectiveness, and compliance with legislation of their products.

Therefore, the future commercialization of the LIFE-NEWBIES technology is a great step in the direction toward public acceptance. Not to mention the positive effects of enhancing circularity and closing nutrient cycles.

But before that, the Resource Recovery team believes they can further improve the concept. A new PhD position opened to broaden the scope – why stop at nitrogen if we can also recover potassium and phosphorus.

Also, the current technology can be improved further; Kuntke: “There is still potential for increased energy efficiency and to make NEWBIES more durable. Scaling is still an issue, albeit less than before, and there are ample nitrogen-rich sources we still can explore.”

LIFE-NEWBIES is a collaboration of:

Evides, ICRA, W&F Technologies, and Wetsus

The LIFE-NEWBIES project has received funding from the LIFE programme of the European Union under grant agreement Nº LIFE17 ENV/NL/000408.

Read more:

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newbies.eu/

BAoBaB

sustainable saltwater battery

To be carbon-neutral in 2050, the world must change more than just its energy generators. Our sustainable power must be drawn from somewhere on cold and windless nights. The EU-project BAoBaB succeeded in making a pilot-scale battery based on salt and water to power the world durably and safely in times of otherwise unavailable supply.

Sustainable storage

Great leaps in solar and wind energy are already yielding a bright future. Though, to be carbon-neutral in 2050, we require gigawatt-scale renewable power. However, these new forms of energy come at a cost – we have no control over the power supply. Energy harvest on windless cloudy days is low, and the weather does not account for demanding seasons. And the opposite also applies – excess energy is today wasted due to the lack of storage options.

To profit from renewable energy, we therefore must store the energy. Current batteries might be able to accomplice such feats, but sustainable alternatives are in dire need. The abundance of resources of local origin is another significant limiter in the evolution of energy storage.

The concept of an *acid-base flow battery* was already introduced in the ‘80s, yet for a long time membranes simply were inadequate for real applications. Now that membrane technology has made remarkable progress, a consortium has successfully taken on the challenge of upscaling and demonstrating this promising battery in the real world.

The heart of the battery

The idea of an acid-base flow battery is built on the principles of bipolar membrane electrodialysis and its reverse counterpart. By using special membranes, water from an incoming salt solution is split into protons and hydroxyl ions, creating an acidic and alkaline solution. In this way, the excess electricity from solar panels or wind turbines is used to generate a pH gradient, which is the driving force of the flow battery. As the acid and alkaline solutions are stored in separate tanks, the amount of energy can be stored for long period (days or weeks), without the risk of self-discharge. By recombing the acid and alkaline solution again, the battery discharges similarly.

“At the heart of this technology is the bipolar membrane,” says researcher Ragne Pärnamäe. She researched suitable membranes for the project. “Current commercial bipolar membranes are designed for producing acid and alkali, not for recombining the two solutions. But for the acid-base flow battery both processes are equally important.”

Here laid the challenge for the Wetsus scientists. “It was like a scientific playground,” says the BAoBaB project coordinator Michele Tedesco, “we had to test all sorts of commercial membranes but concluded that we needed a newly designed one to achieve the targets of the project.”

One such breakthrough was using a new technique to fabricate the membrane. Where usually bipolar membranes consist of two polymeric layers – one positively and one negatively charged –, the Wetsus team investigated a new method to entangle both polymers in a three-dimensional spun membrane, where the water-splitting abilities increased considerably over the traditional 2D ones.
Thanks to the combined efforts and expertise of all partners, the project hit its goal. Starting with a single-cell lab-scale battery (5x7 cm), to a final pilot with 170 m^2 of total membrane area installed, i.e. a x20,000 scale-up factor in just four years. The final demonstration prototype was installed in Pantelleria – an Italian island – with a nominal power of 1 kW and a capacity of 7 kWh. A successful global first of this technology on a pilot scale.

Promising developments
Though the technology is limited in its energy density as of now, the acid-base flow battery will find its niche. Pärnamäe: “It is perfect for community-level energy storage – as a back-up power source for a neighborhood, for example. Especially because it is the safest battery you can find. If it breaks and starts leaking, it will only spill salty water.”

Further promising developments await. The European Innovation Council Accelerator Programme has recently awarded AquaBattery with funding to bring the technology to the market. This EU agenda supplies monetary means to start-ups to scale the technologies they develop for game-changing innovations. A rewarding recognition to further develop their green battery and commercialize it. With the first steps already being set – together with Waterschap Rivierenland AquaBattery launched a pilot at the wastewater treatment plant in Gorinchem.

And here at Wetsus, the focus has drifted towards the bipolar membranes that are at the core of the acid-base flow battery. Tedesco: “Bipolar membranes have so many more applications. We are now investigating the use of such membranes for all sorts of novel applications – like CO_2 capture, wastewater treatment, and further energy storage.” The researchers at Wetsus have gained state-of-the-art insight into these highly-engineered membranes that will further combine scientific excellence with commercial relevance.

Although there are many more solutions to our climate change troubles, and there is more to learn, the acid-base flow battery is already promising us a sustainable future.

BAoBaB is a collaboration of:

Fujifilm, AquaBattery, CIRCE, the University of Palermo, SMEDE S.p.A., and Wetsus

BAoBaB
BLUE ACID/BASE BATTERY

Read more:

Pärnamäe, R., Gurreri, L., Post, J., van Egmond, W. J., Culcasi, A., Saakes, M., … Tedesco, M. (2020). The acid-base flow battery: Sustainable energy storage via reversible water dissociation with bipolar membranes. Membranes, 10(12), 409. *https://doi:10.3390/membranes10120409*

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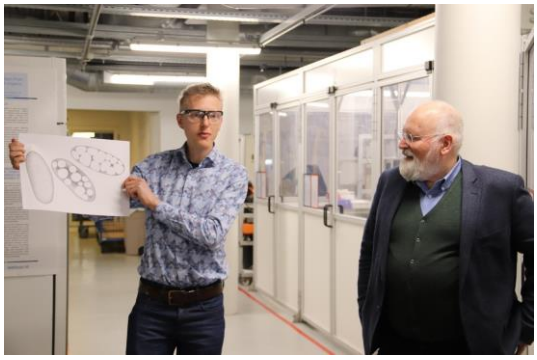
baobabproject.eu

SCALIBUR

Your organic waste can be turned into a biobased and biodegradable thermoplastic materials



More than 75% percent of used plastics end up in landfills or in the incinerator. Even though efforts to recycle fossil plastics must improve, the future will need supply chains of renewable counterparts. Polyhydroxyalkanoates (PHA) are thermoplastic materials with great potential since they can have similar properties as fossil-based plastics, can be made from organic waste, and can be biodegradable to leave zero pollution. The Wetsus theme Biopolymers from Water and its partners in the EU project SCALIBUR managed the plastic's production enhancements and set up a plant to test applicability.

Troubles at the source

As we move away from fossil plastics and into the realm of renewable resources, we are still challenged by troubles of the source. Current commercial PHA production is based on sugar-fed monocultures. Although circular, this is not ideal in all aspects. Cost is a natural contributor to resistance to PHA market entry for traditional plastic producers and consumers. More importantly, the current method of creating the polymer is in direct competition with food production.

However, the Biopolymers from Water theme work with ideas where costs do not have to limit PHA potential. All kinds of bacteria can generate the biopolymer, and they like to eat what organic waste naturally ferments to – volatile fatty acids. In fact, one can grow such bacteria from waste treatment. Bacteria-rich waste sludge from wastewater treatment plants can be fed with fermented organic-rich sludge, wastewaters, or organic residues to produce a lot of PHA polymers.

Once extracted and processed, market applications have to drive the value chain economy. But to test and explore applications, kilogram amounts of PHA are typically required for meaningful testing and process trials.

Scaling up the micro-process

Build a PHA production pilot reactor in a relevant up-scalable context that paves the way with innovative methods and processes for industrial-scale PHA production. This was the first challenge given to researcher Erik de Vries. "I was involved in every step – from design to running the system. This pilot has allowed Wetsus to test the PHA production and develop an efficient up-scalable process." "We are blessed by a wonderful tech team, of course, and in this case, especially Jan and John have been of tremendous help," says Werker.

Theme coordinator Alan Werker who has dedicated years to the ins and outs of producing PHAs, explains: "If we want to push the innovation to the market, we need to root ideas and to learn within a context of meaningful supply chains – the specific input: wastes as raw materials. A goal is to motivate to establish value chains for at least 5000 tons PHA/year for strategic specialty valued products and services." At that level, economies of scale are sufficiently large, and entrepreneurs that dare to develop disruptive market applications can rely on the biopolymer supply and its quality.

Getting to a consistent polymer quality is a challenge in fundamental science, engineering, and tacit know-how. Unlike synthetic plastics, you cannot always work your way up to the desired polymer properties. Instead, the bacteria are *coached* to craft the polymer to be of a particular composition and molecular weight. And the purification step is also a way to prepare desirable properties. A skill set is involved and developed with insights made during the project to produce and formulate polymers with desired properties.

Another challenging goal is the ambition to meet the criteria for food-grade plastics. "When we started out, the idea raised a few eyebrows," says theme manager Alan Werker. "The idea that something generated from *waste* could make it into food contact applications is a foreign concept to many, but much learning can be gained along the way." The idea of refuse as the raw material source plagues our concerns. Resource recovery can only happen if waste is seen with its – sometimes hidden – values.

PHA produced at Wetsus already meets many of the criteria for food-grade applications, yet we are not entirely there. "We are talking about trace quantities – milligram levels for specific impurities per kilogram polymer," De Vries says. Among these residual levels of substances are natural fatty acids that come from the bacteria making

the PHAs and are still mobile in the polymer matrix. Werker: “For a plastic, fatty acids can be a property enhancer of added value. It can improve polymer mechanical properties of toughness. But if it is mobile, it can also slowly diffuse out of the polymer.” Regulations for food-grade applications are very strict about migrating substances.

Werker: “Ironically, people do not mind using oil-based packaging. While everyone is aware of the devastating effect it has on the environment.” We all know of the classic images of oil-drenched birds that have to be rescued, yet this is forgotten. Traditional plastics come from a toxic goo much worse than municipal organic waste.

The future
Luckily, views are shifting. Based partly on the technology and know-how developed at Wetsus, a demo plant is designed and built in Dordrecht, producing tens of kilograms of PHA per week.
Parallel to upscaling efforts, research will continue. De Vries: “Because of our state-of-the-art infrastructure, we were asked to be part of Agro2Circular, another European project that focuses on agricultural waste. We will tailor ways to recover a PHA produced from fruit and vegetable waste.

Developments will take place to optimize the production process, and another point of focus will be applications of the polymers. This will come in the form of two more PhD positions for the theme. Werker: “We are advancing on researching fundamental principles and ideas for innovation on bioprocess engineering, downstream processing, and polymer science.” However, the SCALIBUR polymers already seem to offer insight into ways to reach a good combination of strength and toughness compared to commercially available PHA. De Vries: “the journey continues to understand blend strategies along with refinements on polymer purity, but we already look for niche applications.

This project received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement Nº 817788

Read more:

wetsus.nl/research-themes/biopolymers-from-water/
phario.eu
Scalibur.eu
Agro2circular.eu

Want to see more water technology? Join, learn and network on September 19, 20, 21 and 22.
The global water technology sector will get together in Leeuwarden, capital of water technology, the Netherlands. During the second European Water Technology Week (EWTW 2022), business and innovation leaders from companies, universities and governments will meet and inspire each other. EWTW 2022 features the Wetsus Congress 2022, an international business program initiated by Water Alliance, the assembly of the Global Water Tech Hub Alliance and an exhibition and networking floor. For the program details and sign-up, follow this link: ewtw2022.eu

EUROPEAN WATER TECH WEEK LEEUWARDEN 2022 Connecting Global Water Tech Hubs September 19 - 22