Phosphorus recycling – valuable materials from sewage plants

Modern agriculture relies on phosphorus in the form of chemical fertilisers to provide plants with vital nutrients. However, huge amounts of this valuable raw material end up in our sewage plants. Two new methods to recover phosphorus from wastewater could potentially contribute to the sustainable use of phosphorus in the not-too-distant future.

Phosphorus is a basic building block of life, however it is not found free in nature, but usually in minerals such as phosphates. Phosphates are a component of DNA, they are found in our bones and are energy carriers (ATP) in cells. Countless phosphate ions circulate in the natural cycle between living beings, water and soils. Phosphoric acid peps up coca-cola and phosphate increases the shelf-life of sausages. Most of the phosphorus ore extracted in open pits is, however, used for producing mineral fertilisers. Germany does not have its own phosphate resources, so all 100,000 tons of phosphate rock used annually in Germany need to be imported. Major exporting countries such as Morocco and Jordan are located in politically unstable regions, which is why the European Commission decided in May 2014 to include phosphate on the list of 20 critical raw materials.

In Germany, the phosphates contained in municipal wastewater could potentially meet a large proportion of agricultural requirements. Most phosphate, which is absorbed by plants from the soil and taken up by animals and humans with food, is excreted and ends up in the sewage treatment plants. Many phosphorus recycling methods concentrate on recovering phosphate from sewage sludge or from ashes that remain after the combustion of sewage sludge. These solid phases contain fairly high amounts of phosphate. However, the phosphate can usually only be recovered using chemicals, which is a relatively costly process. The direct application of sewage sludge on fields is controversial because it can pose a danger to animal and human health due to the heavy metals, pathogens and drug residues it contains. Switzerland prohibited this practice in 2006. The German Federal Environment Ministry is currently working on the amendment of the German Sewage Sludge Ordinance. The draft foresees banning the application of sewage sludge on fields from 2025 and making phosphorus recycling mandatory for sewage plants.

New ways of phosphorus recycling

Scientists from Stuttgart, Karlsruhe and Würzburg have developed two new methods that enable the recycling of phosphate to be integrated into the wastewater treatment process of sewage treatment plants. These methods are used to recover phosphate from the liquid phase. The P-RoC (phosphorus recovery from waste and process water by crystallisation of calcium phosphate) developed by the
Competence Centre for Material Moisture (CMM) at the Karlsruhe Institute of Technology (KIT) can be used to recover phosphate from sludge water that results from the dewatering of sewage sludge.

The P-RoC method uses a calcium silicate hydrate granulate, mineral material from the building material industry, for the crystallisation of phosphate. After drying, the granules can be used directly as a fertiliser without requiring further processing. “The exciting thing is that this method does not require any other substances apart from the crystallisation material and it takes relatively little technical effort,” says Rainer Schuhmann, director of the CMM. As far as the contamination of the fertiliser granules with heavy metals, organic pollutants and pathogens is concerned, the granules have been shown to be harmless. At present, the method can recover up to 60 percent of sludge water phosphates and has already been successfully tested in several sewage treatment plants.

Microsubmarines sieve the wastewater

However, the sludge water used in the P-RoC process contains only about 30 percent of all wastewater phosphorus. This is why another method, developed by researchers from Stuttgart and Würzburg, is already being used in the main stream of sewage plants. This particular method uses special composite particles as phosphorus scavengers. These particles move like tiny submarines through the wastewater and collect phosphate ions. They do this so effectively that 99 percent of all phosphate has attached to their special surface after 20 minutes. Shortly after, the particles, along with their valuable cargo, are captured by a magnetic field and transferred into a pan containing aggressive sodium hydroxide solution. At a pH of 13, the tiny submarines release their phosphate cargo and are ready for a new collection round.

Karl Mandel and his colleagues at the Fraunhofer Institute for Silicate Research in Würzburg developed the sophisticated structure of the “microsubmarines”. The composite particles consist of magnetite nanoparticles embedded in a silicon dioxide matrix. These particles are attracted by an external magnetic field and released again when the magnetic field is turned off. However, they do not remain permanently magnetic to avoid clumping together. The particles are 20 micrometres in size, which ensures that they are not released into the environment in an uncontrolled way.

Screening for the best binding properties
Once the basic structure was developed, the Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA) had the job of working out the optimal coating for phosphate ions to bind effectively. Asya Drenkova-Tuhtan is an engineer at the ISWA and explains: “In the current project, we have studied more than 50 different materials and found that so-called layered double hydroxides (LDH) are the most suitable for the intended purpose.” LDH were chosen because they are excellent phosphate absorbers. In addition, they are excellent phosphate desorbers, which means that they easily release phosphate ions into a sodium hydroxide solution.

The researchers' favourite was an LDH consisting of zinc-iron-zirconium (Zn-Fe-Zr) and chose Zn-Fe-Zr LDH coated magnetic particles for further characterisation and application. “The great thing is that...
producing the particles is relatively cheap. Magnetic separation and chemical regeneration of the particles enables them to be reused, so that phosphate can be successfully recovered. The particles can be reused around 50 times,” says Heidrun Steinmetz, Professor of Sanitary Engineering and Water Recycling at the ISWA. In the experimental hall of the teaching and research treatment plant at Stuttgart University, the method will now be taken to the next level: one kilo of microparticles will be used to recover phosphate from more than 6,000 litres of wastewater.

Sewage plants as recycling centres

The researchers are now looking for industrial partners for the industrial implementation of the process. The potential is huge. Coated with suitable LDHs, the microparticles are also able to capture other valuable materials – heavy metals such as mercury and copper – from industrial wastewater. The P-RoC method can be used to recover phosphate not only from sewage water, but also from milk processing plants, manure and green waste.

Our wastewater therefore has the potential to become an important raw material collection point.

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