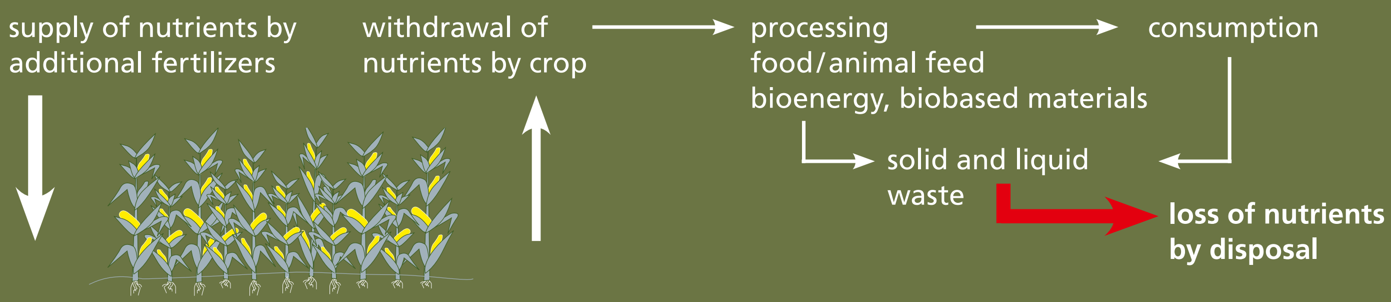
Fraunhofer IGB

FRAUNHOFER INSTITUTE FOR INTERFACIAL ENGINEERING AND BIOTECHNOLOGY IGB

RECOVERY OF PLANT NUTRIENTS FOR A SUSTAINABLE AGRICULTURE

TRADITIONAL NUTRIENT FLOW



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NUTRIENT RECYCLING

FOR A SUSTAINABLE USE OF NUTRIENTS IN AGRICULTURE

Nutrients such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and sulfur (S) are essential for all living organisms, in particular for plants. Thus, these nutrients are the main components of fertilizers, and therefore indispensable for the world's food supply. Nowadays, these nutrients are only partially recycled in agro-ecosystems, since human intervention has created a linear, dispersive system.

Nutrient flow

The nutrient flow begins by adding nutrients as fertilizers to the soil. The plants take up these nutrients, which are then withdrawn from the local plant-soil ecosystem by harvesting. The harvested plants are then used for the production of food, animal feed, bioenergy and biobased materials. Once these products are consumed, the nutrients are mostly lost in the established waste disposal systems, as these materials are not returned completely to the soil. Currently, only a fraction of these nutrients are returned to the soil in the form of manure, digestate and compost. To compensate this gap in the nutrient cycles, mineral fertilizers must be produced and constantly applied to the soil (Fig. 1).

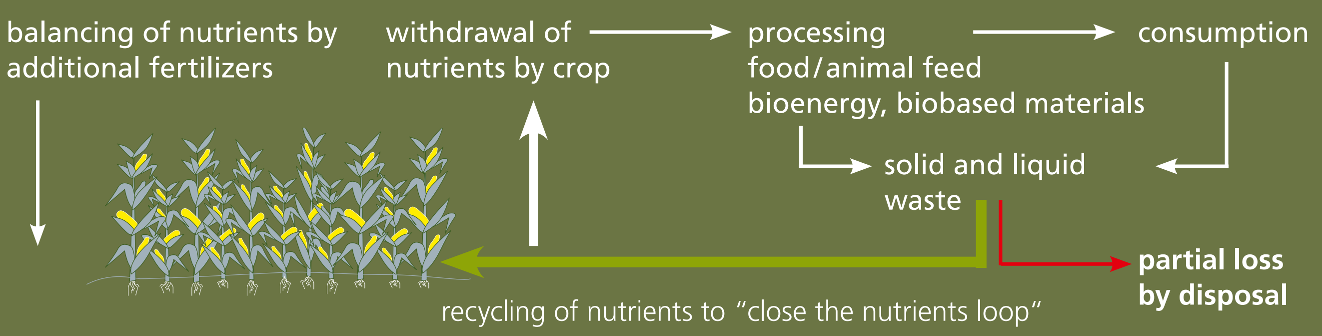
Industrial fertilizer production

The industrial production of today's mineral fertilizers is based on non-renewable raw materials. In the case of phosphorus, the main source for fertilizer production is phosphate rock. Unfortunately, the phosphate rock reserves are decreasing rapidly worldwide and its purification is a highly pollutant procedure[1].

Phosphorus is an element that is indispensable for life, which cannot be manufactured, synthesized, or replaced by any other element. In contrast, nitrogen is almost endlessly available from the atmosphere. Nitrogen fertilizers are synthesized using the Haber-Bosch process, which transforms gaseous nitrogen from the air to ammonia (NH_3). However, this production of synthetic NH_3 requires a high consumption of energy (about two percent of the worldwide energy production is needed) and is based on non-renewable natural gas using about five percent of its global consumption[2]. As energy costs rise continuously, the cost of producing these fertilizers rises as well.

With the growing world population, the demand for food, bioenergy and biobased materials will continue to increase, which in turn will lead to a higher demand for fertilizers. As a consequence, the prices for fertilizers will rise, which will cause a decrease in farm production, higher food prices, growing food insecurity and rising social and economic challenges that the next generations will have to face.

INNOVATIVE CIRCULAR NUTRIENT RECYCLING



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Loss of nutrients

Paradoxically, as we run out of raw material for fertilizer production, large quantities of nutrients are lost in the sewage system with further energy consumption. The state of the art in most municipal wastewater treatment plants is to remove nitrogen compounds like ammonium (NH_4^+) and nitrate (NO_3^-) from wastewater by nitrification/denitrification processes. In this highly energy-consuming process, these compounds are converted to gaseous nitrogen that just escapes into the air.

Phosphate is removed by a chemical precipitation with aluminum or iron salts. Aluminum and iron phosphates cannot be used as fertilizers because they are not plant-available and could also release iron and aluminum in concentrations toxic for plants. According to estimates, worldwide approximately 4.3 million tonnes of phosphorus are lost in this way per year[3].

Overfertilization

Agricultural soils are often overfertilized with mineral fertilizers. This leads to a further drain of nutrients into surface- and groundwater, causing water pollution such as eutrophication. Land application of animal manure and fermentation residues from biogas plants also causes nutrient losses. These residues have an unfavorable nutrient (N:P:K) ratio that is not optimal for the growth requirements of various crops. The requirement is calculated with reference to one nutrient (normally nitrogen), which results in an overdose of the other nutrients in the soil. The uncontrolled application of nutrients from organic fertilizers results – especially in areas with intensive livestock husbandry – in nutrient oversaturation, which is harmful to the environment.

1 *General nutrient flow in a non-sustainable system.*

2 *General nutrient flow in a sustainable circular system.*

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[1] Cordell, D., Neset, T. S. S. and Prior, T. (2009) The phosphorus mass balance: identifying 'hotspots' in the food system as a roadmap to phosphorus security. Current Opinion in Biotechnology

[2] Smith, Barry E. (2002) Nitrogenase reveals its inner secrets, Science 297 (5587), pp. 1654–1655

[3] Dockhorn, T. (2009) About the economy of phosphorus recovery. Conference proceedings: International Conference on Nutrient Recovery, Vancouver, Canada

Our approach:
Sustainable nutrient management

The key response to this lack of sustainability within agriculture and waste management is to recreate a cycle of nutrients (p. 3, Fig. 2). For this reason, Fraunhofer IGB is developing and implementing sustainable, cost-efficient technologies and strategies for the integrated management of resources.

One of the key areas is the development of new technologies for recovering nutrients from wastewater and organic waste. In the last years, various solid and liquid wastes (e.g. residues from olive oil production, livestock husbandry residues and wastewater) have been characterized and evaluated to determine their nutrient content and to define their potential recycling strategies.

Our service: Development of process chains from recovery to application

In our implemented processes, nutrients are precipitated or pelletized so that they can be marketed by industrial partners as a full-fledged and specific product. We can also mix our products to obtain a nutrient composition to suit the type of plant and the soil conditions.

Fertilizer can be applied as a solid, but also as a liquid formulation. We provide the possibility of developing various formulations, manufacturing and characterizing small batches and sample amounts.

1 *Recovered struvite from wastewater that can be used directly as a slow releasing fertilizer.*
2 *Pellets from digested residues of the olive mill production that can be used directly as organic fertilizers.*
3 *Foliar fertilization.*


1

ePHOS®

ELECTROCHEMICAL PROCESS FOR PHOSPHORUS RECOVERY

One of the most advantageous approaches to recover phosphorus from wastewater is the crystallization of Phosphorous (P), Nitrogen (N) and Magnesium (Mg) as struvite (magnesium-ammonium-phosphate: $MgNH_4PO_4*6\ H_2O$). In state-of-the-art struvite precipitation processes, the limiting reactant magnesium must be added as a solution of $MgCl_2$, $Mg(OH)_2$ or MgO. Furthermore, the pH value has to be raised to a range between 8.5 and 9.5, usually by adding sodium hydroxide.

Fraunhofer IGB has developed and patented a novel electrochemical process to recover ammonium (NH_4^+) and phosphate from the filtrate water resulting from municipal wastewater treatment. In the ePhos® process phosphate (PO_4^{3-}) and ammonium are precipitated electrochemically – without any use of chemicals as magnesium-ammonium-phosphate ($MgNH_4PO_4*6\ H_2O$, MAP or struvite).

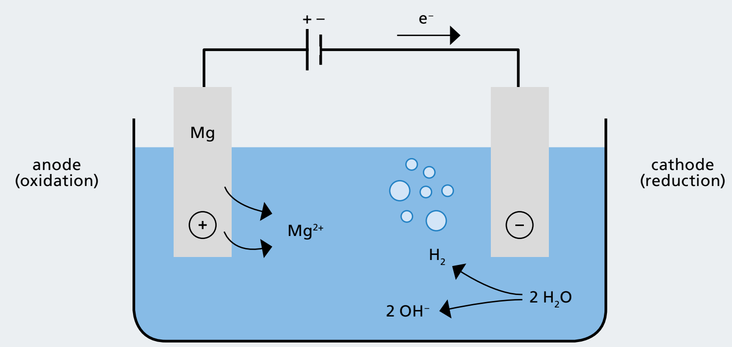
High-quality fertilizer struvite

The recovered product struvite can be used directly in agriculture as a high-quality, slow releasing fertilizer. Struvite was tested in plant-pot experiments showing excellent results. Plant yield and plant nutrient-uptake with struvite were up to four times higher than with commercially available mineral fertilizer (calcium ammonium nitrate and triple superphosphate). This result demonstrates that struvite is easily plant-available and has a positive effect in plant growth.

Process principle

The electrochemical phosphorus precipitation takes place in an electrolytic cell consisting of a cathode and a sacrificial anode of magnesium.

Water molecules are split by the cathodic reduction forming OH^- ions and hydrogen (H_2). OH^- ions raise the pH value of the wastewater which remains constant at pH 9. As a result, it is not necessary in the ePhos® process to adjust the pH value by dosing chemicals (bases) for the precipitation process. Oxidation occurs at the anode: magnesium ions are released into the solution and react with the phosphorus and nitrogen in the water to form struvite.



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Feasibility study in a pilot plant

In the course of a feasibility study the process was tested using a pilot plant with a flow rate of up to 1 m^3/h at a sewage treatment plant with biological phosphorus elimination. The average phosphorus elimination rate from the centrate water of the digested sludge dewatering and the phosphorus conversion to struvite was more than 80 percent. The phosphorus concentration in the centrate water was reduced by an average of 180.0 mg/L to 20.8 mg/L. The phosphorus load that no longer has to be treated when the filtrate water is recirculated, decreases by 37 percent; this amounts to 9284 kilograms annually and results in a reduction of sludge production by 7 percent. The design of the process for the client's plant shows that the electrochemical phosphate precipitation would require approx. 10 tons of magnesium in the form of sacrificial electrodes per year. From this, approx. 73 tons of struvite per year would be obtained which can then be used directly as a fertilizer. The total quantity of chemicals that would have to be used at the treatment plant would decrease by 40 tons or 20 percent per year.

Industrial-scale implementation with flat-panel reactors

With the results from the first pilot tests, in which tubular electrolytic cells were used, the process was further developed with flat-panel reactors for industrial use.

Advantages

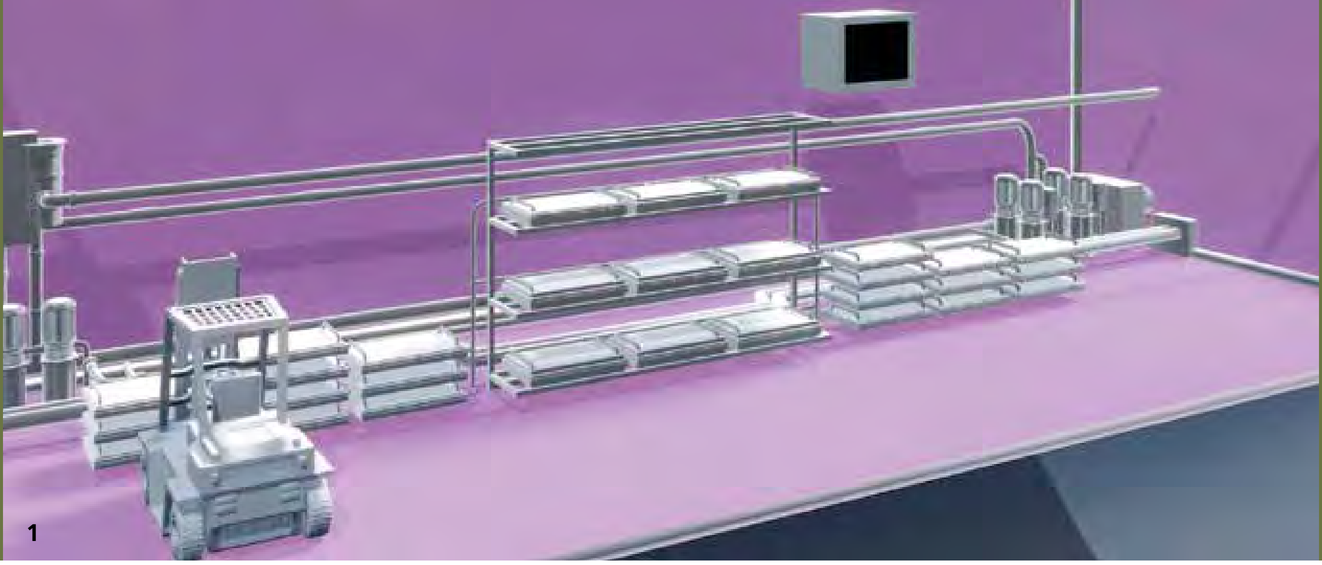
The ePhos® plant concept is based on the series connection of electrolytic cells in parallel. As this is a purely electrochemical process, the cells or cell pathways can be switched on or off by a process control system depending on the demand. This beneficial mode of operation and the efficient, chemical-free operation represent unique selling propositions that insure competitiveness.

Energy consumption for operating the electrochemical precipitation process proved to be low (0.78 kW h/m^3 wastewater).

1 *Recovered struvite crystals under scanning electron microscope.*

2 *Principle of the electrochemical struvite precipitation process.*

3 *Mobile pilot plant for struvite precipitation.*



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Market introduction

A licensing agreement with the US company OVIVO, an established supplier of water supply and distribution equipment and systems, covering markets in the USA, Canada, and Mexico has been signed. The motivation for investing in the new phosphorus recovery technology resulted from the new, extremely low discharge limits for phosphorus in the USA.

The ePhos® plant enables sewage plant operators to combine wastewater purification with the value generating production of fertilizer. Moreover, the precipitation process is also suitable for sectors such as the food industry where the wastewaters are rich in ammonium and phosphate. In the future, further ammonia recycling process modules will be added to the ePhos® process in order to achieve sustained cycle management of the nutrients at sewage treatment plants.

1 *Visualization of industrial-scale ePHOS® plant.*
2 *Soil degradation.*
3 *Residues from the olive oil production.*


2


3

NUTRIENT RECOVERY FROM AGRICULTURAL RESIDUES

Land application of animal manure, digestate from biogas plants and other agricultural residues supply agricultural soil with valuable organic matter and essential nutrients that help to meet crop nutrient requirements and maintain soil fertility[4]. However, in regions with intensive livestock production, land application is not always possible because of the already high nutrient content of the soil. For instance, in a conventional agricultural biogas plant with 500 kW_{el}, approximately 100 tonnes of nitrogen (N) per year are generated with the digestate. If a fertilization of 170 kg N per ha is used, then 588 ha are needed for that quantity of nitrogen[5]. Thus, in regions with intensive livestock production, this digestate and surplus manure must be either transported to other areas with nutrient demand or stored for long periods.

Reduction of soil organic matter

Moreover, due to the dramatically increasing interest in the production of biobased products and bioenergy, soil degradation is becoming a serious problem in Europe. In recent years, several areas of forests and grasslands have been converted into agricultural land. This results in loss of soil fertility, carbon and biodiversity, lower water-retention capacity, and disruption of nutrient cycles[6]. At the moment, the decline of soil fertility is only masked by the overuse of synthetic fertilizers without the replacement of organic matter. However, in the longer term, the reduction in soil fertility will impact on food security, especially taking into account that soil is a non-renewable resource.

Hence, Fraunhofer IGB is developing technologies to recover nutrients and organic matter from agricultural residues as high-quality and compact organic and mineral fertilizers[7].

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[4] Stoll, M. S. et al. (2012) Evaluation of treated manure as fertilizer. Proceedings of the 8th International Conference ORBIT 2012; Rennes, France June 12 – 15, 2012

[5] Fuchs, W. and Drosg, B. (2010) Technologiebewertung von Gärrestbehandlungs- und Verwertungskonzepten, pp 10. Universität für Bodenkultur Wien, Vienna, Austria

[6] Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions – Thematic strategy for soil protection (2006)

[7] Soil. European Commission: Environment http://ec.europa.eu/environment/soil/index_en.htm Access Date: February 10, 2012

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Pilot plant for processing of livestock manure

Pig manure contains valuable plant nutrients, mainly nitrogen and phosphorus, and indigestible feed solids such as plant fibers. In the EU-funded project BioEcoSIM (grant agreement no 308637), a project consortium with 15 partners from 5 countries have succeeded in using pig manure as a valuable resource. Coordinated by Fraunhofer IGB, different processes to convert the constituents of livestock manure into high-value fertilizers were developed and integrated as separate modules within a single pilot plant. This makes it possible to treat the manure directly at its place of origin.

Every hour the plant processes for demonstration purposes 50 kilograms of pig manure to about 500 grams of mineral phosphate fertilizer, 500 grams of mineral nitrogen fertilizer (ammonium sulfate), as well as 900 grams of organic biochar.

Combined processes

In a first step, manure is pretreated to dissolve phosphorus completely and separated by a coarse filtration into a solid and a liquid phase. The solid phase is then dried using a process developed at Fraunhofer IGB; this works with superheated steam in a closed system and therefore achieves a high energy efficiency (p. 12). After that, the dried organic components are converted to organic biochar at over 300°C by a pyrolysis process – in an atmosphere of superheated steam, as in the drying step. Microorganisms are completely destroyed in the process.

The liquid manure fraction has a high concentration of dissolved inorganic nutrients. As a first step, phosphorus is recovered in a precipitation reactor and then separated as phosphate salts by filtration. Secondly, nitrogen is recovered using a membrane cell. Ammonia dissolved in water diffuses across the membrane and is recovered as crystalline ammonium sulfate. The remaining liquid contains only traces of phosphorus and nitrogen, but is rich in potassium, which is ideal for irrigation purposes.

Advantages and outlook

Extensive investigations and field studies have shown that the mineral fertilizers and organic soil conditioners made from livestock manure can be used directly in agriculture as readily available fertilizers and humus-forming substrates. Finally, the mass of the dewatered and processed products makes up only about four percent of the original volume of livestock manure. The process will be further developed for mass production.

Soil improver from residues of olive oil production

In the project En-X-Olive funded by the European Union (grant agreement no 2184442-2) we researched together with partners from Spain, Italy, Greece and France the recovery of biogas, polyphenols, and fertilizers from residues of olive oil production (p. 9, Fig. 3). The objective of the work package fertilizer recovery was to produce a compact organic soil improver from the digested residues of the olive oil mill industry. The digested residues were separated into their solid and liquid fractions and the solid fraction was dried and pelletized. The product was a competitive commercial fertilizer that could be stabilized, stored, transported and spread with common fertilizer spreaders used in agriculture (p. 4, Fig. 2).

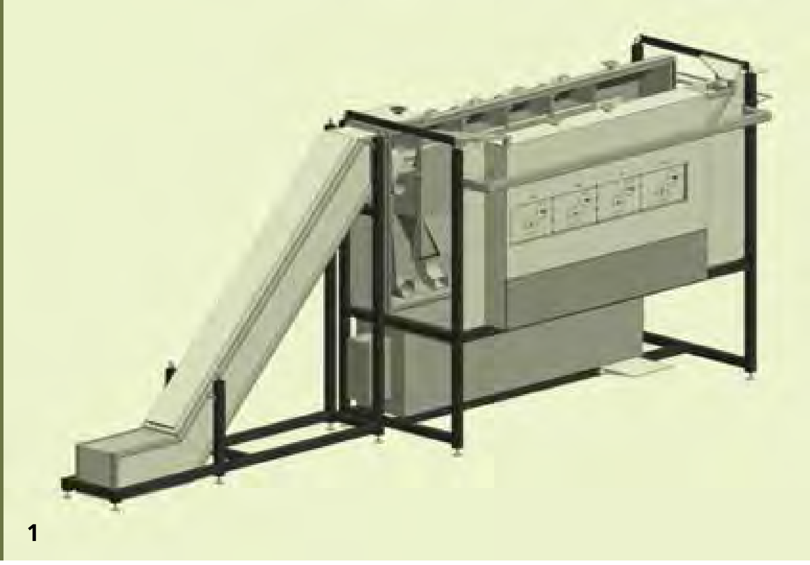
Fertilizer pellets for organic farming with insect repellent activity

More and more frequently, customers are buying organic vegetables, because these products are not treated with pesticides or laden with chemicals. However, if these plants are attacked by pests, farmers have few options to protect them. For instance, organically-grown cabbages are often plagued by the cabbage root fly, the common enemy of such plants, causing great damage to crop yield.

However, farmers will soon be able to repel these flies reliably – and will therefore be able to proceed with their organic farming practices. In the EU-funded EcoBug project, Fraunhofer IGB together with colleagues from the University of West Hungary and the Research Institute Nortek in Oslo – on behalf of various organic agriculture associations – have produced pellets with combined fertilizer-repellent properties for the organic farming of cabbage (grant agreement no 218467-2). The pellets consisted of dried digested manure with 0.1 percent dried cyanobacteria. If the pellets are applied to freshly planted vegetables, then the cyanobacteria are degraded by the soil flora and release a scent that repels cabbage root flies. The nutrient-rich digestate additionally fertilizes the plants. The pellets are easy to apply, and the nutrients are directly available to the plants.

The fertilizing and repelling effect of this product was confirmed in open field trials in Hungary and Spain. Our project partners in both countries achieved highly satisfying results: white cabbage plants that were fertilized with the combined pellets grew significantly better than non-fertilized plants. None of the plants fertilized with the combined pellets in the field trials were infested with the cabbage root fly.

1 *BioEcoSIM pilot plant.*
2 *Mineral phosphate fertilizer, mineral nitrogen fertilizer and organic biochar.*
3 *Fertilizer and biological pest repellent all in one: EcoBug pellets, made from the residues of cow manure fermentation enriched with cyanobacteria.*



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Drying of organic residues and cyanobacteria with superheated steam dryer

In the EcoBug project, the drying of the digested manure and cyanobacteria was carried out with a novel superheated steam dryer (SHSD). This drying process offers significant advantages in comparison with common hot or cold air dryers. Due to the superior heat transfer of steam, higher drying rates are achievable with SHSD at the same temperature. This leads to a lower specific energy consumption of 0.75 – 0.90 kW h / kg water removed for SHSD compared to 1.10 – 1.70 kW h / kg water removed in a comparable hot air dryer[8]. Moreover, higher thermal conductivity and heat capacity of superheated steam compared with hot air results in enhanced heat transfer to microorganisms, enabling pasteurization or sterilization. As superheated steam is recirculated and reheated in a closed loop, an excess of evaporated water develops which is carried off along with NH_3 and volatile organic carbon (VOC) from SHSD. In our approach VOCs and NH_3 are condensed out with the excess steam enabling condensable valuable organic substances including volatile fatty acids (VFA) and NH_3 to be recovered. This eliminates the environmental problem of VOC and NH_3 emissions in conventional hot air dryers.

Recovery of organic phosphorus for enhanced phosphate precipitation

Phosphorus is found in many organic residues as both inorganic and organic compounds. These phosphorus compounds may be very stable in nature. The phosphorus dosage can therefore hardly be controlled by direct application of manure or fermentation residues. This frequently results in an over-application of phosphorus on soil, which has negative environmental and economic consequences. The natural biological decomposition process converts these organic compounds into inorganic plant-available ions (NO_3^-, NH_4^+, PO_4^{3-}). However, this process can take several months or years, as it depends on the specific local conditions such as humidity, temperature, precipitation, the activity of microorganisms, etc. At Fraunhofer IGB, we have developed analytical methods for the characterization of organic residues in regard to their phosphorus content. Moreover, we are developing biocatalytic processes for the mineralization of organic phosphorus in agricultural residues and its recovery as a valuable fertilizer.

8 Desai, D. K. et al. (2009) Superheated steam drying of Brewer's Spent Grain in a rotary drum, Advanced Powder Technology 20 (3), pp. 240 – 244

Formulation and stability studies of leaf fertilizers

Plants can be fertilized in two ways: through their leaves and the soil. Unlike fertilization of soil, the so-called foliar fertilization permits the targeted and precise dosage of various nutritional elements at a fixed time without the influence of soil nutrient fixation and washing-out. Nutrients are sprayed in a diluted form directly onto the leaves of the plant and absorbed by it. Not only macro-nutrients (N, P, K, Ca, Mg and S) are used for foliar fertilization, but also micro-nutrients, e.g. manganese, iron and trace elements. All of these nutrients contribute beneficially to plant growth.

For an industrial client, Fraunhofer IGB examined the ideal composition of leaf-fertilizers on the basis of natural raw materials. The main goal was to find the right proportion of agent and substrate to avoid side-reactions. Furthermore, stability studies were carried out to guarantee that the products are stable (2 years) according to CIPAC (Collaborative International Pesticides Analytical Council). The products can be certified with EU Eco-Regulation 834/2007.

Extraction of plant strengtheners

Besides fertilizers, "plant strengtheners" are increasingly widespread in agriculture. These compounds do not have a fertilizing effect, but they contribute to the nutrient uptake of plants. Moreover, plants are verifiably more resistant to pest infestation and pathogenic organisms. For these reasons, plant strengtheners – especially when they are made from in-artificial substances – are a reasonable and ecological alternative to classical pesticides and herbicides.

For another industrial client, Fraunhofer IGB has studied the extraction of natural raw materials as plant strengtheners. Stability studies of the product were carried out after finding the ideal extraction conditions.

1 *Superheated steam dryer.*

2 *Bioreactor for biocatalytical recovery of organic phosphorus.*

3 *Examination in the laboratory.*

OUR SERVICES

R&D Services

- Chemical and physical characterization of raw materials and residues with regard to their nutrient content
- Development of strategies and technologies for optimum recovery of nutrients and organic matter
- Modelling of processes, statistical experiment design, laboratory experiments, reactor design and scale-up
- Feasibility studies, including experimentation with our struvite plant and superheated steam dryer
- Thermodynamic and kinetic analysis of the precipitation of different salts for the assessment of competitive reactions
- Formulation and processing of multicomponent fertilizer from liquid and solid residues with repellent properties
- Production of organic liquid fertilizer and plant strengtheners by means of extraction and suspension processes
- Stability and altering studies of liquid fertilizer according to CIPAC

Equipment

- Laboratories with equipment for extraction and dispersion experiments as well as for stability experiments of liquid fertilizer
- Apparatus for the online particle measurement and characterization of crystals (1 µm – 2.5 mm)
- Superheated steam dryers for testing and demonstration purposes (SHSD)
- Pelletizing machine
- Mobile demonstration plant for the precipitation of struvite and other inorganic salts

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Fraunhofer IGB brief profile

The Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB develops and optimizes processes and products in the fields of health, chemistry and process industry, as well as environment and energy. We combine the highest scientific standards with professional know-how in our competence areas – always with a view to economic efficiency and sustainability. Our strengths are offering complete solutions from the laboratory to the pilot scale. Customers also benefit from the cooperation between our five R&D departments in Stuttgart and the institute branches located in Leuna and Straubing. The constructive interplay of the various disciplines at our institute opens up new approaches in areas such as medical engineering, nanotechnology, industrial biotechnology, and environmental technology. Fraunhofer IGB is one of 69 institutes and independent research units of the Fraunhofer-Gesellschaft, Europe’s leading organization for applied research.

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