

# FINAL REPORT

UQ00061

## Fertilizer from Wastes Phase II

### PROJECT DETAILS

**PROJECT CODE:** UQ00061

**PROJECT TITLE:** FERTILIZER FROM WASTES PHASE II

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### Summary

The project focused on demonstrating technologies to recover nutrients (nitrogen (N), phosphorus (P) and potassium (K)) from waste, as well as determining the agronomic value of the recovered products. Novel anaerobic digestion (AD) technologies enabled improved P recovery. The novel process of electro dialysis (ED) was also developed as a competitive proposition for N and K recovery. Nutrient recovery technologies were optimised and demonstrated at a pilot scale on waste water. The recovered nutrients were tested and opportunities were identified. The project enables generation of renewable fertilisers from waste, and secures a sustainable source of nutrients for the grains industry in Australia.

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## Conclusions

The project addressed its goals and demonstrated opportunities to recover renewable fertilisers from waste streams and showed the potential of these products for grain growers.

Struvite crystallization was demonstrated as being relatively cost effective, compared with conventional P removal, and with pay back periods of 5-10 years. Specifically, the project enabled application to a broader range of waste industries, and developed short hydraulic retention time (HRT) crystallization as a viable low capital alternative. The trials were successful in recovering more than 90% of the P as struvite fertiliser.

## Recommendations

Economic and practical advantages of struvite precipitation have been demonstrated, but full scale implementation of this technology is limited due to its emerging status, limited market for struvite, and conservative nature of the Australian waste industry. Further work is recommended to engage end-users and technology providers, creating a market for struvite and providing incentive for full scale implementation of this technology. This can be done by demonstrating the benefits of formulated waste derived struvite in different crop and soil varieties and by subsidising full scale trials. There is a growing incentive for the end-user to reduce nutrient loads in waste streams due to increasingly stringent regulation around discharge limits. During this project, several end-users and technology providers have been engaged with the technical and economic brief of the technology.

The ED project is novel and was developed in this project. The laboratory scale experiment, pilot scale demonstration and mechanistic model confirmed the feasibility of the process to concentrate nutrients, particularly N and K, from wastewater. It has clear application in its original embodiment and an N and K recovery process, and this will be further developed with commercial partners. However, it has become evident that it has broader application as a general recovery platform (e.g. for higher value complex organics), and further research should be done to develop these areas.

AD technologies were developed and optimised to improve P solubility and release nutrients from waste streams which are currently being disposed. The goal was to improve nutrient availability and capture through the nutrient extraction technologies developed in this project. The application of these technologies was limited, for example, the anaerobic membrane bioreactor was applied on meat processing wastewater, low pH AD on domestic wastewater, and leach bed AD

on spent litter. Further testing on different waste streams is recommended, along with further process optimisation to improve resource recovery and economics. Details of these were provided in reports and publications of the respective technologies.

Product development on the recovered nutrients is recommended, particularly for the ED concentrate, due to presence of organics and high salt content in the product. The availability of P from struvite can be further improved, through product formulation and developing conditions. It is critical to evaluate the performance of these products on Australian soils for different crop varieties to engage end-users and grain growers for future development of these technologies.

## Outcomes

The project has delivered an alternative, viable framework to enable full scale implementation of technologies to recover macro nutrients. It is expected that the technology developed through this project will allow for long term independence of agriculture from mineral fertiliser, with enhanced medium term buffering against price movements. Further economic, environmental and social benefits are expected post-project through large scale implementation of these technologies and commercial application of the renewable fertilisers.

**Economic benefits:** Grain growers in Australia will benefit with access to low cost, continuously viable, and well formulated renewable fertilisers. There is potential for long term international trade in mineral fertiliser. For intensive agriculture waste generators, and domestic wastewater industries, these technologies enable an economic way to reduce nutrient loads and revenue from product sale, with payback of 5-10 years for most waste streams. Nutrient recovery at a national level will buffer international price fluctuation.

**Environmental benefits:** Nutrients from waste streams in Australia are currently discharged in solids streams such as manure and biosolids, in large water bodies and/or in atmosphere through biological processes. There are concerns on direct application of solid wastes and wastewater to agriculture, and losses to the environment due to cost, presence of contaminants, pathogens and its long-term influence on soil salinity. Renewable mineral fertilisers are contaminant and pathogen free, provide opportunities to reduce nutrient load in waste streams, and reduce environmental costs of manufacturing fertilisers. Nutrient recovery will enhance the long term sustainability of the Australian grains industry.

**Social benefits:** Nutrient use has always been a linear cycle, from manufacturing to disposal, while this project provides an alternative which is more acceptable to the public. It also enables local manufacture of majority import (N, P), and complete import (K) commodities. The concentrated form of the renewable fertiliser will reduce negative social impacts such as truck movements. The anaerobic technologies developed in this project will reduce the social burden of disposal of large volume and odorous sludge produced at waste facilities.

## Achievements/Benefits

Fertiliser is one of the most significant on-farm input costs (approx. 25%) for modern agriculture, with the majority of N and P imported, and almost all K imported. The grains industry is one of the largest users of fertiliser in Australia, and an alternative source of nutrients would reduce reliance on imported fertilisers, and buffer against international price instability. Recycling nutrients from waste streams provides access to low cost fertiliser and long term sustainability to growers. Phase I of the project (2010/2011) identified strong opportunities to further develop nutrient resources from the Australian agro-industrial waste streams and their potential for processing into mineral fertiliser products. Nutrient recovery was found very compelling for economic reasons, especially when combined with energy recovery. It also provides an additional revenue stream to intensive agriculture, while reducing greenhouse gas (GHG) emissions, and providing a competitive, renewable P stream. Phase II was focused on further developing these opportunities, with specific areas targeted that would increase both the quantum and economic feasibility of nutrient recovery.

The key objectives of the project were to:

1. Demonstrate nutrient recovery technologies at a pilot scale.
2. Develop novel nutrient recovery technologies.
3. Product testing.

Specific achievements for each objective are provided below:

#### 1. Demonstrate nutrient recovery technologies at a pilot scale

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) recovery was identified as an emerging technology with broad applicability. Struvite crystallization was demonstrated on industrial wastewater (Manildra, New South Wales (NSW)), treated sewage wastewater (Queensland Urban Utilities, Queensland (QUU QLD)) and meat processing wastewater (Teys Australia, QLD and Northern Cooperative Meat Company LTD, NSW). The trials were jointly funded by these industrial partners. Most of the trials were performed for at least six months onsite. The trials were successful in recovering more than 90% of P as struvite fertiliser and achieved an effluent concentration of 50mg/L of calcium (Ca) and K in the wastewater resulted in Ca and K based precipitants in the product, with a reduction in P concentration. Where high organic suspended solids were present in the input, this resulted in a high organic fraction in the product, again, with a loss of P content. Pre-treatment of the input wastewater, either via settling or micro filtration, improved the product quality and reduced the presence of organics in the recovered product. Trials using magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) resulted in excess dosing of Mg and the recovered product had a high concentration of Mg. Longer residence time (more than 24 hours) was required where  $\text{Mg}(\text{OH})_2$  was used to improve Mg solubility, while the typical reactor was operated with a short residence time (0.5hr) using magnesium chloride ( $\text{MgCl}_2$ ) as a Mg source. The project identified that short HRT crystallization followed by granulation was a competitive process to the more commonly applied (and high capital) commercial in-reactor granulation processes currently present in the market, with good economic viability for P and N recovery on a range of waste streams.

ED as a novel recovery technology was a product of this project, and had proceeded from concept to pilot as part of the project. A 45L ED pilot system with 30 cell pairs was commissioned in May 2016 to recover ammonium ( $\text{NH}_4^+$ ) and K from the struvite crystallizer effluent produced at the QUU Innovation Centre. The ED unit had wider flow channels (6mm), compared with current commercial industrial application, to avoid possible clogging due to the presence of suspended solids in the wastewater. This configuration was based on fundamental research done in the laboratory. The process was optimised onsite for different current density. The recovery rate of the pilot scale reactor was similar to the laboratory scale reactor, 0.11kg N/m<sup>2</sup>/d at 20 A/m<sup>2</sup>. Energy consumption is substantially less than for conventional N manufacturing (1% N and more than 0.2% K), and highly competitive with existing methods of side stream treatment.

#### 2. Develop a number of novel technologies to enable and improve nutrient recovery, including low pH AD (specifically for P), application of new digester technologies, and development of the ED process.

One of the key targets identified was improving P solubility during AD in order to enable better recovery post-digestion. Various conditions were tested, including low pH, chemical additives, and high pressure. Batch and continuous AD was conducted at different pH conditions (pH 5.0-7.7) using sewage waste activated sludge as substrate. Soluble P concentrations could be increased by a factor of three at low pH conditions (pH less than 5.5) compared with high pH, with substantially deteriorated reactor operation (pH less than 6.2). The average performance in terms of methane yield and organic solids conversion reduced linearly with decreased pH conditions. Similar results in terms of P solubility and biological performance were observed in both batch and continuous study. The loss in capability could be related to a shift in microbial community, with acidogens dominating at low pH (less than 6.0), while methanogens decreased by 88% at pH 5.5 compared to neutral pH.

Apart from the loss in methanogenic and hydrolytic capacity, continuous acid dosing to maintain low pH condition was identified as a key limitation. To assess an alternative method to avoid acid dosing, a continuous anaerobic digester was operated under pressure at 1-6 bar absolute pressure, which would enable an increased  $\text{CO}_2$  concentration to both depress pH, and enable P solubilisation due to chemical interactions. The soluble P concentration increased linearly with the applied pressure - it was 55% more at 6 bar. The specific methane yield increased by 40% compared to the control (1 bar), but volatile solid destruction and chemical oxygen demand (COD) removal was unaffected, indicating better gas capture. Increased pressure caused a substantial change in archaeal populations, without substantial change in function. Chemical additives were also tested to avoid acid dosing and increase soluble P concentration during AD. The chelating agents and ion exchange resins were selected to specifically bind Ca and Mg, and thereby increase the availability of P in the digested solution. This was uneconomic due to the high cost of the chemicals.

Emerging anaerobic technologies, such as leach bed and anaerobic membrane bioreactor (AnMBR), were developed and co-funded by end-users to treat piggery and meat processing waste. These bioreactors were demonstrated at a pilot scale and were effective in removing organics from waste as biogas and conserved nutrients for extraction processes. The AnMBR trials

have been conducted with two different meat processing wastewater treatments. It consistently removed more than 95% of COD from the wastewater at both sites, with achievable hydraulic retention times of 24-48hrs. The struvite recovery trials were successful using the AnMBR effluent and consistently 90% or more P removal was achieved. The leach beds were operated on digestion of spent straw bedding from swine or pigs, to assess the effects of hydraulic configuration (trickling and flood-and-drain). Results showed that digestion performance was insensitive to hydraulic configuration. Post digestion tests suggested that the leach beds may be inhibited by microbial diversity or biological inhibition. Overall, the leach beds demonstrated good potential for digesting agricultural residues, and there is a future need to improve overall digestion performance.

ED was developed to recover N and K as mineral fertiliser from wastewater streams. Additional funding from Grains Industry Research Scholarships (GRS10661) was secured to fund a PhD student on fundamentals. This resulted in a process model suitable for design and application of commercial processes, as well as extensive results based on fundamentals which led to the pilot application. The laboratory scale experiments were focused towards understanding competitive transport of cations, optimise pilot scale operations and estimated parameters to feed into the mechanistic model. For synthetic solutions, faster flux ( $\text{kg m}^2/\text{d}$ ) were observed for monovalent ions than for divalent ions following the order  $\text{K}^+ > \text{NH}_4^+ > \text{Ca}_2^+$ . Interestingly, the flux for divalent ions was not affected by commercial monovalent membrane and was highly dependent on the initial concentration of the ions. The laboratory scale ED reactor was further operated on pre-treated centrate from sewage treatment plant wastewater. The ammonia concentration in the product stream increased and achieved plateau concentration (8g/L) over 160hrs. The current efficiency achieved was 70%-80%, while the recovery rate was  $0.2\text{kg N/m}^2/\text{d}$  at current density of  $53.3\text{ A/m}^2$ . Precipitation was observed on the ion exchange membrane, due to presence of P, but this was eliminated by using centrate treated with struvite crystallization and by operating the product stream at low pH. Based on results from both laboratory and pilot work, commercial value has been established and talks are underway with two commercialisation partners to take the technology to market.

Due to the relatively low value of commodity fertilisers, particularly for N, and hence relevant to the ED product, a scoping study was conducted to upcycle waste derived N to produce high value nitrogenous products. Nitrogen can be processed via chemical synthesis, biosynthesis and electro-synthesis to produce amines, amino acids, proteins, intermediates, agro-chemicals, animal feeds and fuels. The review identifies research gaps, evaluates future potential for application of these technologies and outlines paths and barriers for adoption of these technologies. There is a need to apply, demonstrate and prove these proposed technologies on wastewater N to move these beyond their current infancy.

#### Product testing

Struvite was granulated and was tested for field and pot application with various grain crops. The struvite granulation was optimised to produce 2-4mm size granules using 10% citric acid as a binding agent. This represents a lower capital, potentially lower operating cost alternative to existing processes which rely on in-reactor granulation. Field trials of the granulated struvite were done on wheat and canola crops at various locations in QLD, NSW and Western Australia (WA). There were mixed outcomes in terms of plant nutrition, but overall the crop yield was lower for the struvite crops compared to commercial P fertilisers. Pot trials were performed at the University of QLD (UQ) using different sources of P: Waste derived struvite (WDS), synthetic struvite (SS) and mono calcium phosphate (MCP) on maize. The WDS was derived from domestic wastewater using  $\text{Mg}(\text{OH})_2$ . The plants treated with the WDS had no P response and the plant heights were similar to the control. While the plant growth treated with SS was significantly higher than WDS, it was lower than MCP at the similar application rate. The presence of residual  $\text{Mg}(\text{OH})_2$  in WDS was found to inhibit the growth of the maize. The results suggest that residual  $\text{Mg}(\text{OH})_2$  in struvite is inhibitory and reduced P release from the fertiliser treatment. Further work is required to improve P availability from struvite. The project identified implication of struvite forms as P nutrition for the grains industry. A pot trial was done using the ED concentrate as an N source and compared with liquid urea. The trial was conducted on sorghum using potting mix at a UQ greenhouse. No significant difference in plant height, dry biomass and nutrient concentration was observed between the ED concentrate and liquid urea trial, indicating ED concentrate is an effective replacement.

## Other research

The major benefit of this project is the identification of low risk and economically promising nutrient extraction technologies. The following research and development (R&D) opportunities were identified during the project:

- a) Piloting and development of ED technology.

The work developed an ED process for N and K from domestic wastewater, which is low cost and low footprint compared with competing emerging processes. Opportunities were identified to extract charged organics from high strength coloured wastewater through this technology. This will be further developed as a joint industry research project. Further research is required on process optimisation to reduce operating and chemical costs, test a wide variety of wastewater and develop novel ion exchange membranes to improve product recovery yield. The work involved in piloting and further optimisation would accelerate the commercial success of GRDC investment and grain growers will benefit from the renewable fertilisers.

b) Develop novel processes to recover high value nitrogenous products from wastewater.

Current N recovery technologies are largely focused on producing low value products such as fertiliser and salt, and hence it is becoming increasingly difficult to justify the economy of such technologies. Nitrogen in wastewater can be upcycled to produce high value products, such as agricultural chemicals, amines, proteins, industrial chemicals, nutritional food, and animal feed. This needs to be further developed and demonstrated at a laboratory scale to assess process feasibility and economics.

c) High pressure AD offers a clear method to improve P recovery, with other potential process benefits, including higher product methane content, and enhanced digester performance. However, the high cost of pressure reactors is not likely to justify the benefits at this point. Hence, the digester manufacturing industry should be contacted to identify whether there is a route to market for pressurised AD.

d) Product development and testing. There is further scope for product formulation and testing of new generation fertilisers recovered from the technologies developed in this project. A formulation is needed to create balanced fertiliser and improve nutrient availability for plant uptake, possibly through blending with other fertilisers, sorbers or bacteria. Phosphate solubilising bacteria particularly could be imbedded in struvite to resolve the P solubility issue identified in this project.

e) Next generation fertilisers. These are focused on low cost of manufacture, sustainability of supply, improved crop response, and reduced environmental dissipation. The two major fertilisers developed from this project (struvite and ED concentrate) clearly fit into this class, and opportunities within the larger area of next generation fertilisers should be further developed.

## Intellectual property summary

Struvite crystallization: There is commercial opportunity with process equipment and configuration flexibility developed in this work, but currently no intellectual property (IP) is attached. Several end-users and technology providers have been engaged with a technical and economic brief.

ED: The project partners hold a patent on this technology and two technology providers have been engaged to further develop and commercialise this technology.

Anaerobic technologies: End-users have been directly engaged with the development of anaerobic technologies, particularly for membrane and leach bed bioreactor.

Renewable products: Fertiliser companies have been consulted regarding marketing and commercialisation of new waste derived products.

## Additional information

### Attachment

Detailed list of publications as journal articles, patent, conference papers, and industrial reports.