



NEPTUNE

New sustainable concepts and processes for
optimization and upgrading municipal wastewater
and sludge treatment

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Deliverable 2.2 · New approaches for a sustainable WWTP design

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1 Introduction

Within WP2 in the Neptune project, promising technologies were developed and further investigated for sustainable wastewater treatment, where wastewater is regarded as a resource rather than a waste. These technologies comprise **bioelectrochemical systems** for energy recovery, denitrification and production of value-added products. Two technologies were developed for the removal of micropollutants; i.e. **ferrate oxidation**, which can be used for the combined removal of pharmaceuticals and phosphate, and **biogenic manganese oxides**, which permit both the chemical and biological removal of pharmaceuticals. Phosphorus and heavy metal recovery with **pyrolysis** and **biopolymer production** from sewage sludge are two techniques developed for sludge revalorization.

The previous deliverable 2.1 “**Novel technologies for wastewater and sludge treatment**” described the above-mentioned technologies in detail. An up-to-date picture of these novel technologies was provided with new insights obtained during the Neptune project

In this deliverable 2.2 “**New approaches for a sustainable WWTP design**” the applicability of these technologies to a wastewater treatment system is discussed. Information on where and how these processes could fit into a wastewater treatment plant (WWTP) of the future is provided in relation to the technologies’ advantages and limitations and estimated costs if available.

2 Novel technologies in a WWTP design

In order to move from a conventional activated sludge (CAS) system to the WWTP of the future, three issues related to improved process sustainability were targeted in the Neptune project:

- Micropollutant removal
- Energy recovery to reduce CO₂ emissions
- Sludge valorisation

Figure 1 visualizes how one or several novel technologies investigated in the Neptune project could fit in this WWTP of the future. By substituting the FeCl₃, normally dosed at the end of the treatment to precipitate PO₄³⁻, by **Ferrate** (Fe(VI)) a wide range of highly persistent micropollutants can be removed together with phosphates. The application of **biogenic manganese oxides** (BioMnOx) can also prevent further contamination of our water bodies and aquatic life by micropollutants. With BioMnOx it is possible to remove pharmaceuticals both chemically with manganese oxides and biologically with manganese-oxidizing bacteria.

As seen from Figure 1, energy recovery is an important part of sludge valorisation. By pretreating the waste sludge from primary and secondary settling, the biosolids become a suitable resource for **biopolymer production** and a feedstock for **bioelectrical systems** (BES). Sludge valorisation is achieved via the production of bioplastics and value-added products while also attaining biosolid stabilization. At the end of the sludge line, **ultra high temperature pyrolysis** can provide nutrients and energy recovery by producing clean syngas as well as solid product suitable for phosphorus recovery and safe final disposal, due to the low content of heavy metals and organic micropollutants. Energy recovery is aimed by combining **bioelectrical systems** (BES) and anaerobic digestion. The latter also serves as an alkalinity source to increase the buffer capacity of the BES-feed. The conventional technology of anaerobic digestion completes the picture of energy recovery because the pretreatment and biomass processing within biopolymer production render biosolids more attractive to anaerobic digestion due to higher biogas production.

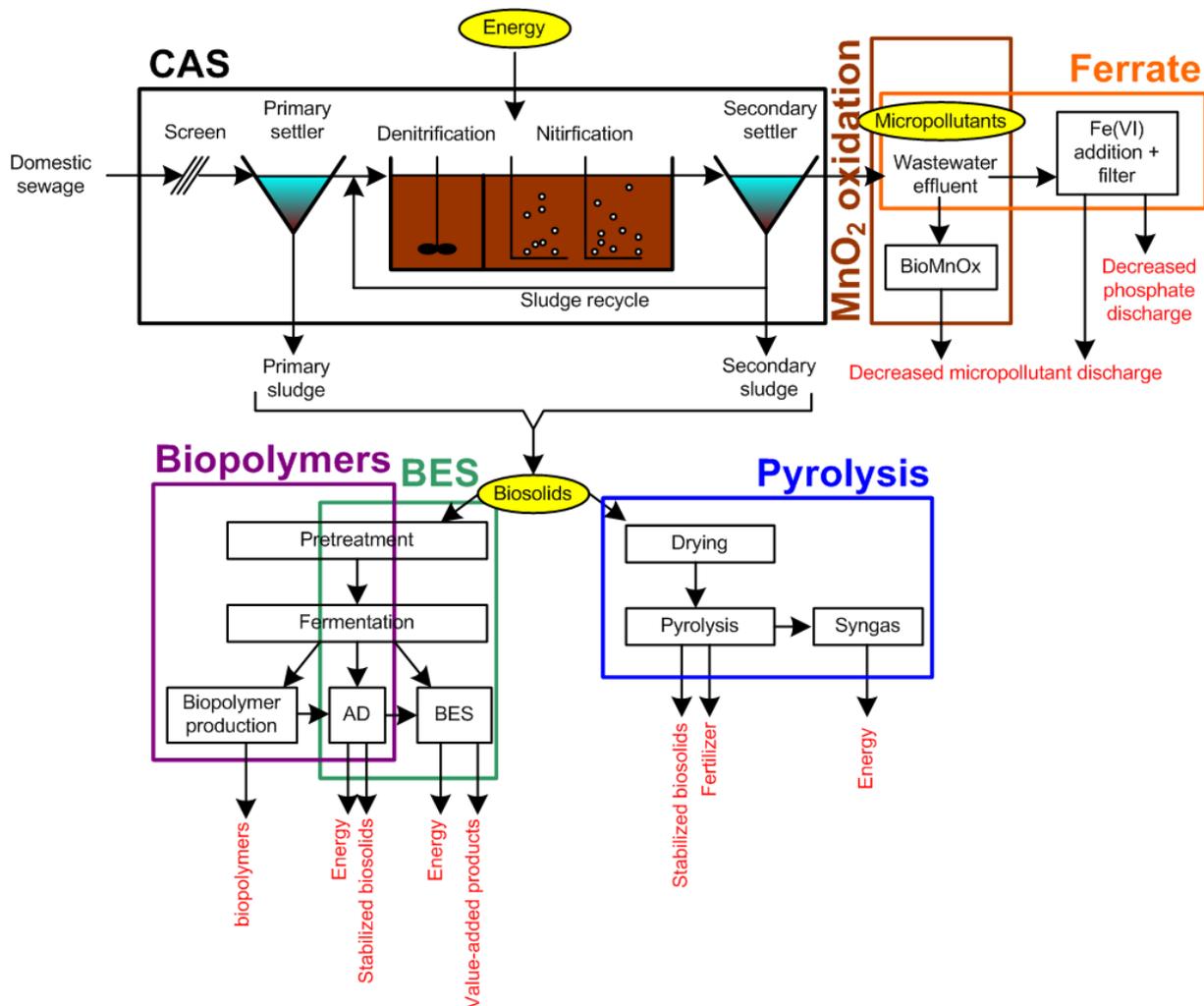


Figure 1 Overview of the technologies (Biopolymers, Bioelectrical systems (BES), Ferrate, MnO₂ oxidation with biogenic manganese oxides (BioMnOx) and pyrolysis), investigated in the Neptune project for the improvement of the sustainability of a Conventional activated sludge (CAS) system.

3 BioElectrochemical Systems

3.1 BioElectrochemical Systems and Sludge Treatment

BioElectrochemical Systems (BESs) represent a new approach to wastewater treatment. While wastewater treatment has traditionally focused on nutrient removal, research nowadays focuses on finding combined solutions for wastewater treatment and energy/resource recovery. BESs have recently gained considerable attention as they enable direct conversion of the chemical energy of electron donors, such as waste organics, into electrical energy (Logan et al., 2006). The system can generate useful power while, for example, treating a wastewater stream. It is also possible to provide net power to the reactor, in order to produce value-added products at the cathode. The process description and technology applicability have been previously outlined in Deliverable 2.1.

Whilst pilot-scale demonstrations to date have focussed primarily on using wastewater from brewery and pulp and paper treatment facilities, there is interest in evaluating the potential of sewage biosolids as a feedstock. Biosolids describe the sludge by-products produced by sewage treatment plants and constitute a burden for the operation of wastewater treatment plants since sludge handling and disposal represent a major operating cost. Biosolids have traditionally been viewed as an uninteresting BES feedstock due to the high concentration of suspended solids and the high viscosity of the process stream. However, the research conducted under Neptune has successfully showcased the opportunity for the beneficial use of biosolids as a feedstock for BESs. The generation of energy has been demonstrated in a reproducible fashion in laboratory-scale reactors fed with waste activated sludge (WAS) pretreated via high-pressure thermal hydrolysis and fermentation (see Figure 2). Furthermore, by optimising the ratio of pretreated WAS with an on-site source of alkalinity (i.e. anaerobic digester effluent) to increase buffer capacity, lab-scale reactors fed with real influent perform significantly better than the equivalent synthetic streams. These results ultimately highlight the significant potential of sewage biosolids as a feed stream for a BES and provide a platform to further investigate whether energy generation or the production of a value-added product is suitable.

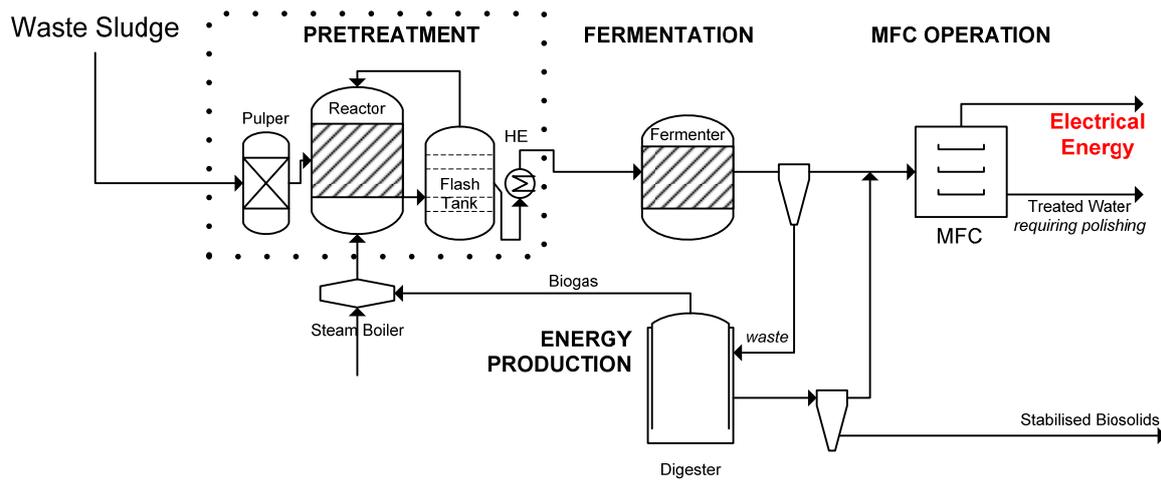


Figure 2 Process flow diagram used in the production of energy in a BES from pretreated waste sludge. The three main sub-processes are: sludge pretreatment, acidogenic fermentation and energy production in a BES operated in galvanic mode. Note that the BES could be operated in electrolysis mode to produce value-added products (e.g. dilute solution of caustic soda and hydrogen peroxide) at the cathode.

3.2 Contribution to Sustainability

A life cycle assessment (LCA) of BES technology was recently performed by researchers at the AWMC (Foley et al., 2009). The study used SimaPro 7 LCA software and ISO 14040 LCA standards to compare three technology options:

- Conventional, high-rate anaerobic wastewater treatment with biogas for co-firing onsite boiler
- BES operated in galvanic mode to produce energy
- BES operated in electrolysis mode to produce 3 wt% hydrogen peroxide solution at the cathode.

The pre- and post-treatment processes were assumed to be the same for all three options, with an assumed influent flow-rate of $2200 \text{ m}^3 \text{ d}^{-1}$ with a COD loading of 4000 mg L^{-1} . Furthermore, the BESs were specified to have a volume of 1228 m^3 and a current density of 1000 A m^{-3} [recently achieved with a litre-scale novel BES reactor design at the AWMC (Rabaey et al., 2009)]. All three options were evaluated over ten years of operation, with the start-up and operational phases considered (de-commissioning phase excluded). Taking into consideration both the first order (i.e. direct atmospheric emissions and effluent discharges) and second order (i.e. emissions plus resources required for upstream energy production and chemicals manufacture) impacts, the study clearly illustrated that BES technology is environmentally competitive with existing anaerobic digestion technology (see Figure 3). The sustainability of BESs operated in galvanic mode will be significantly improved through materials development, in particular the substitution of fluorinated compounds in the ion exchange membrane and the minimisation of stainless steel components. BESs operated in electrolysis mode have a distinct environmental advantage over their galvanic counterparts

due to the displacement of hydrogen peroxide production by the traditional Riedl-Pfleiderer AO Process. It should be emphasised that two key assumptions made in the LCA study have yet to be demonstrated at pilot-scale; (1) current density of 1000 A m^{-3} , and (2) 10 year reactor lifetime. Furthermore, such a LCA analysis has not been performed for a BES being fed with fermented hydrolysed biosolids.

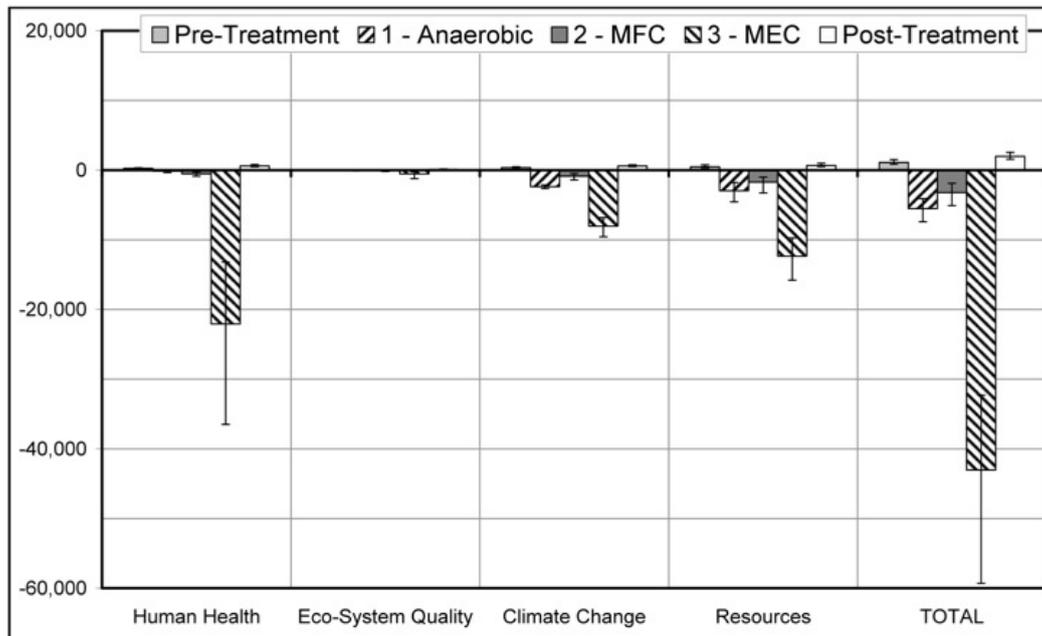


Figure 3 LCA results (y-axis represents the end-point characterisation results for the options normalised by comparing them against the environmental profile of an “average European”, which is embedded in the IMPACT 2002+ LCIA methodology in SimaPro 7)

3.3 Technology Limitations

The technology limitations at lab-scale with synthetic medium include:

- Poor material conductivity
- Poor medium conductivity and alkalinity
- Poor reactor design leading to dead spaces in the reactor due to uneven flow distribution and significant ohmic potential losses due to large dimensions
- pH gradients across the membrane due to ions other than protons (e.g. sodium and potassium) in the medium maintaining electroneutrality in the liquid phase,
- Loss of performance due to the cross-over of chemicals from the cathode
- Loss of performance due to undesired microbial communities on the anode (e.g. methanogens),
- Lifetime performance loss due to scaling of the membrane and poisoning of cathode catalysts by soluble sulfide compounds.

All of the afore-mentioned limitations are also applicable at lab-scale with real wastewater, with the main problem usually being the optimisation of the ratio of organics to alkalinity. This problem is often overcome with the addition of synthetic phosphate buffers, however, this approach is not economically feasible at full-scale. In the work performed during the Neptune project, anaerobic digester effluent has successfully been mixed into the BES influent and performance comparable to the addition of synthetic buffer has been obtained. At pilot-scale, the afore-mentioned problems are supplemented with issues relating to highly variable feed, unreliable pumps, performance loss due to the larger dimensions and problems with designing an electrical control system that can reliably manage such large loads. Further information relating to the technology limitations at pilot scale can be found in a recently published review (Rozendal et al., 2008).

3.4 Current State of Application

Given that BES technology has been shown to handle organic loading rates comparable to competitive technology ($\sim 7\text{-}10 \text{ kg}_{\text{COD}} \text{ m}^{-3}_{\text{reactor}} \text{ day}^{-1}$) and at present has unequalled means to decouple redox reactions, lab-scale studies are being performed to further evaluate how this technology could be applied in different wastewater treatment scenarios. For example, novel processes that are currently being developed include simultaneous COD removal and denitrification, oxidation of recalcitrant compounds in reverse osmosis concentrate and the production of value-added chemicals (e.g. caustic soda, hydrogen peroxide, methane, butanol, biopolymer). In addition to exploring different areas where this technology could be applied in the future, there is significant effort at lab-scale to develop novel electrode and membrane materials for the BES designs that are currently the most economically viable if scale-up could be achieved. Furthermore, this materials work is being supported with modelling and validation work to better understand the sources of BES performance loss and hence provide feedback to continuing reactor design efforts and electronic control system development.

With respect to pilot-scale installations, the AWMC spin-off entrepreneurial enterprise (Bilexys) has recently commissioned a second generation pilot plant onsite at a Fosters Brewery (Yatala, Queensland). The reactor is based on a successful litre-scale laboratory trial with a new reactor design (provisional patent submitted, see Rabaey et al., 2009). The new generation reactor has a significantly smaller footprint in comparison to the first generation set of tubular reactors, and is performing substantially better. This improvement is attributed to a reduction in the size of all of the reactor components, improved electrical connectivity and improved flow distribution. Successful operation of this pilot plant during the

latter half of 2009/beginning of 2010 is expected to attract external investment and expansion of the pilot scale trial to include other industries (e.g. pulp and paper industry).

3.5 Costs

Economic analyses performed by the AWMC together with external consultants have led to a general conclusion that the economic value of energy production by BES technology operated in galvanic mode is small in comparison to the value of the possible value-added products when the technology is operated in electrolysis mode. In either case, the major economic draw-back is the high capital cost of the reactor (approximated at €15000 m⁻³ with current state-of-the-art designs and materials). For example, at current costs, a BES producing hydrogen peroxide would have a payback period of approximately five years (see Figure 4). In order to decrease the high capital cost, several reactor components require significant innovation, including:

- Minimisation of the amount of expensive metal current collector included in the design, and potential material substitution
- Development of significantly cheaper membranes, which is deemed possible with the current cost trend for Asian manufacturers
- Replacement of expensive catalysts at the cathode with non-expensive alternatives, possibly a biological catalyst.

If these cost targets can be achieved and the resultant BES can perform at 1000 A m⁻³ for at least ten years, then the net present value calculation results in Figure 4 illustrate why this technology is attractive in comparison to more conventional wastewater treatment alternatives.

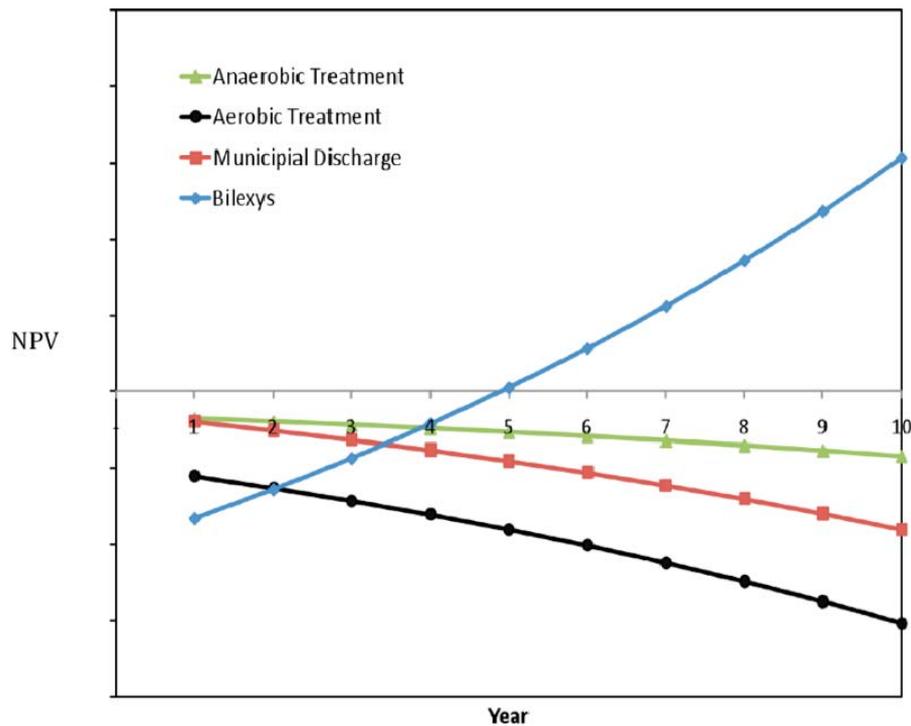


Figure 4 Calculated net present value (NPV)¹ of four technologies for a medium-size brewery: anaerobic treatment, aerobic treatment, municipal discharge and bioelectrochemical system operated in electrolysis mode (Bilexys entrepreneurial venture; assuming reactor capital cost of €15000²)

¹ NPV compares the value of money today to the value of that same money in the future, taking inflation and returns into account. If the NPV of a prospective project is positive, it should be accepted. However, if NPV is negative, the project should probably be rejected because cash flows will also be negative.

4 Ferrate for Micropollutant and Phosphate Removal

4.1 Contribution to Sustainability

Municipal wastewaters have been identified as a major point source of micropollutants such as human pharmaceuticals, personal care products and household chemicals to the aquatic environment. Although wastewater treatment plants are able to remove a suite of micropollutants via sorption to activated sludge or biodegradation, the fraction of polar and persistent organic micropollutants is still constantly released and a potential threat to aquatic life. Mitigation strategies to lower these micropollutants loads within a tertiary treatment step are hence intensively discussed in the scientific community and by regulators. Ferrate can be used as an oxidant and disinfectant and has been shown within the Neptune project to oxidize a broad spectrum of reactive micropollutants in wastewater. So far, no toxic by-products of ferrate are known which would be comparable to those formed by chlorine or ozone. In contrast to ozone, ferrate has the additional benefit of removing phosphate from wastewater by the Fe(III)(hydro)oxides which are formed as a result of ferrate decomposition.

4.2 Limitations

Ferrate solutions are generally unstable although the instability can be retarded at low temperatures, high pH values or by using low ferrate concentrations. Solid ferrate salts are stable but they are costly and contact with water must be avoided. The most convenient approach might hence be to generate ferrate electrochemically *in situ* and to apply it directly for wastewater treatment (Figure 5). Still, the application of ferrate salts is possible as well and should be carefully evaluated.

Electrochemical cell for ferrate production

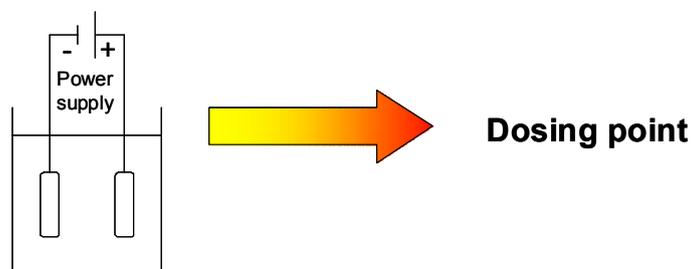


Figure 5 Scheme of an electrochemical cell for ferrate production and addition to the wastewater stream.

4.3 Current State of Application

For wastewater treatment plants already practicing a chemical phosphorous removal, it can be straightforward to switch to a ferrate treatment because the existing facilities for pumping and mixing can be used. However, technologies for on-site production of aqueous ferrate and its rapid application are required. E.g. in case of on-site production of ferrate by the electrochemical method, an electrochemical cell needs to be installed (see Figure 5). Alternatively, off-site production of stable ferrate salts and transport to the application site is possible as well. Accordingly, a safe storage room is needed.

Figure 6 shows possible dosing points for ferrate in a wastewater treatment train. **Addition to secondary effluent in a contact and flocculation tank (no 3) combined with a separation unit is highly recommended** due to the higher stability of ferrate in wastewater with a lower organic matrix load. As an example, Figure 3 shows the relative stability of ferrate in different wastewater matrices with and without activated sludge (i.e. dosing points no 2 vs 3 in Figure 6). Ferrate was consumed within >30 min in the secondary effluent without activated sludge (no 3), whereas in the wastewater with activated sludge (no 2) it was completely consumed in less than 3 min.

A subsequent sedimentation is necessary as it is for chemical phosphorous removal by Fe(II) or Fe(III) salts.

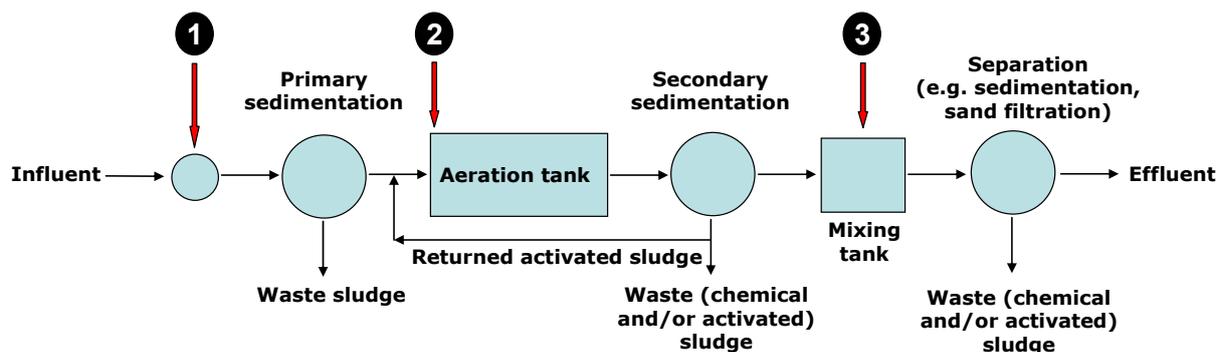


Figure 6 Dosing points for ferrate at a municipal wastewater treatment plant.

Up to now, only laboratory-scale experience is available but ferrate treatment of municipal wastewaters should be tested in pilot-scale plants.

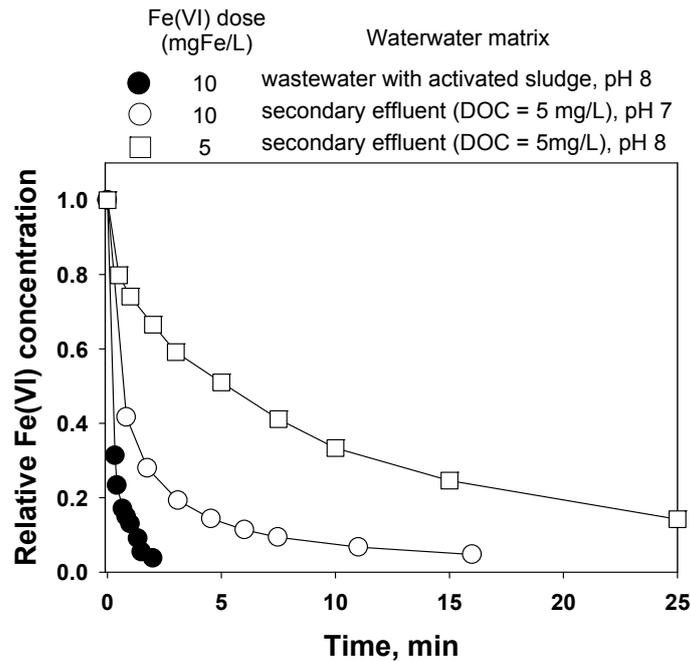


Figure 7 Comparison of Fe(VI) decreases in different wastewater matrices with and without activated sludge (corresponding to the dosing points no 2 and 3 in Figure 6, respectively). Wastewaters were taken from WWTP Dübendorf, Switzerland.

4.4 Costs

The application of ferrate is currently more expensive than the application of ozone since large-scale production of ferrate does not exist yet. The costs for high purity ferrate salts are currently around €12 kg⁻¹, and €0.7-1.4 kg⁻¹ for ozone (comparison based on the molecular weight of Fe(VI) in K₂FeO₄ and ozone). Still, as results for ferrate application for wastewater treatment are very promising, different production technologies should be evaluated. From past experiences with other water treatment chemicals such as ozone, the cost of ferrate may drop significantly with its widespread applications and technical developments. Therefore, in future the costs for ferrate might be similar to ozone (€0.06 m⁻³ wastewater, including both operational and investment costs). However, in a complete cost analysis, the lower costs for additional chemical phosphorous removal as well as the lower investment costs compared to ozone have to be considered as a benefit.

5 Biogenic Manganese Oxides (BioMnOx)

5.1 Contribution to Sustainability: Micropollutant Removal

Several reports show in secondary effluents the occurrence of toxicity, estrogenicity, teratogenicity and genotoxicity originating from the mixture of recalcitrant pharmaceuticals, personal care products, biocides, household and industrial compounds (Aguayo et al., 2004), resulting in sublethal effects for the aquatic organisms. Therefore it is necessary to search for mitigation technologies for wastewater reclamation to protect the aquatic environment.

Ozonation and chlorination have been applied during the last decade for the abatement of pollution cause by the presence of these micropollutants and although they are effective techniques, since only a few micropollutants such as X-ray contrast media and triazine herbicides persist ozonation, there are some drawbacks (production of toxic products, increased overall cost).

Manganese oxides have been applied to remove different kinds of organic micropollutants, including antibacterials and related compounds with phenolic and fluoroquinolonic moieties, aromatic *N*-oxides, tetracyclines, and biocides such as triclosan and chlorophene (Zhang et al., 2008). With chemical MnO₂, low pH is required for adequate removal. In the Neptune project, it was shown that this process is also possible at neutral pH when biogenic manganese oxides are used and *in situ* re-oxidation was possible to prevent loss of the oxidant. Details on the production, mechanism and application of BioMnOx is given in deliverable 2.1.

5.2 Limitations

In non-buffered systems, the pH increases during the chemical oxidation of compounds by BioMnOx until the reaction stops because the increased pH will inhibit the process. Low pH can enhance the oxidation with several orders of magnitude, but below pH 6, no biological re-oxidation by Mn-oxidizing bacteria occurs anymore, which results in the loss of the oxidant. Therefore a subneutral pH of 6.2-6.8 is optimal for the reaction. A pH-adjustment of the STP-effluent is therefore required.

The two key features of BioMnOx are the biogenic precipitated MnO₂ on the cell wall of a 'living' manganese-oxidizing bacterium. The latter is important to re-oxidize the formed Mn(II), to remove its negative effect on the oxidation reaction of the pollutant and to prevent

the loss of the oxidant. Mn-oxidizing bacteria are heterotrophic microorganisms. This implies that they need an organic carbon source for their energy metabolism. The amount of carbon source that becomes available from the oxidation of micropollutants is not sufficient for the maintenance of these bacteria; neither is the metabolic energy from biological manganese oxidation. This has two main implications for the technology. First, it decreases the manganese re-oxidation capacity, resulting in a loss of the oxidant and in a higher sorbed Mn(II) concentration, which negatively influences the oxidation reaction of the pharmaceuticals. Secondly, the biological degradation of reaction products or biodegradable micropollutants decreases when the BioMnOx 'ages'. This drawback is a result of the fact that STP-effluent does not contain high concentrations of assimilable organic carbon.

Not all compounds are eliminated by BioMnOx. Compounds, such as carbamazepine, oxazepam, primidone, trimethoprim, diatrizoate and benzothiazole compounds are resistant towards BioMnOx oxidation.

5.3 Current State of Application

A lab scale continuous operation in a membrane bioreactor (MBR) with BioMnOx in the outer compartment (Figure 8) showed the successful removal of pharmaceuticals in a STP-effluent matrix at ng and $\mu\text{g L}^{-1}$ range. Aeration is necessary for the re-oxidation of the formed Mn(II), and can be applied in an external vessel or directly in the outer compartment of the MBR.

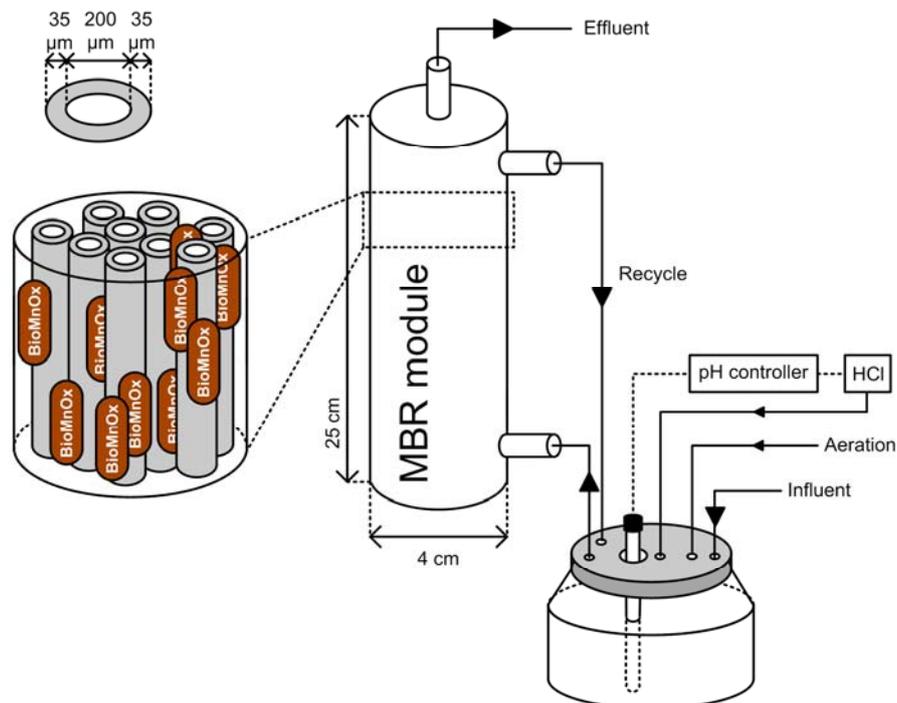


Figure 8 Configuration of the MBR with the BioMnOx hollow fiber module (200 mL) and aeration vessel (150 mL)

Several removal mechanisms are possible in this reactor configuration.

- Chemical oxidation of anti-inflammatory drugs (e.g. diclofenac, ibuprofen and naproxen) and biocides (chlorophene, triclosan and diuron)
- Adsorption of antibiotics (e.g. sulfamethoxazole, erythromycin and clarithromycin) to the manganese oxides
- Biodegradation of analgesics (codeine, dihydrocodeine and morphine) by the manganese-oxidizing bacteria
- Biodegradation by the enriched microbial community in the reactor either through direct metabolism or cross-metabolism during nitrification (iopromide, iomeprol, iohexol, mecoprop, benzonphenone-4, *N*-acetyl-sulfamethoxazole)

Some compounds, detected in the STP-effluent applied in this configuration did not show significant removal and are therefore persistent, e.g. carbamazepine, oxazepam, primidone, trimethoprim, diatrizoate and some benzothiazole compounds. Therefore, this technique can lower the total micropollutant removal, but needs a further treatment in case of drinking water production.

The next step to go to pilot or full scale application would include testing the BioMnOx in a slow sand filtration setup. The biogenic manganese oxides precipitate on available surfaces such as sand grains and a biofilm. In this way, the BioMnOx would be retained in the sand filter. It could be interesting to investigate the BioMnOx treatment as a **pre-treatment** of domestic wastewater before the activated sludge step for BOD removal, since the manganese-oxidizing bacteria would benefit from the bioavailable carbon source for growth and biodegradation and manganese-oxidizing activity.

6 Sludge Pyrolysis

Nowadays, at the most WWTP the mixture of primary and secondary sludge goes to stabilization and disinfection processes if used in agriculture (aerobic or anaerobic digestion, composting, pasteurization etc.) followed by dewatering and drying. The result is stabilized dewatered or dried sewage sludge that has to be finally disposed of. Incineration is still in use as the best alternative for sludge final disposal in terms of hazardous impact reduction and energy reuse. However, more sustainable sludge handling methods have been introduced with constant need for improvement, including ultrahigh temperature Pyrolysis.

The process could be presented with the following scheme.

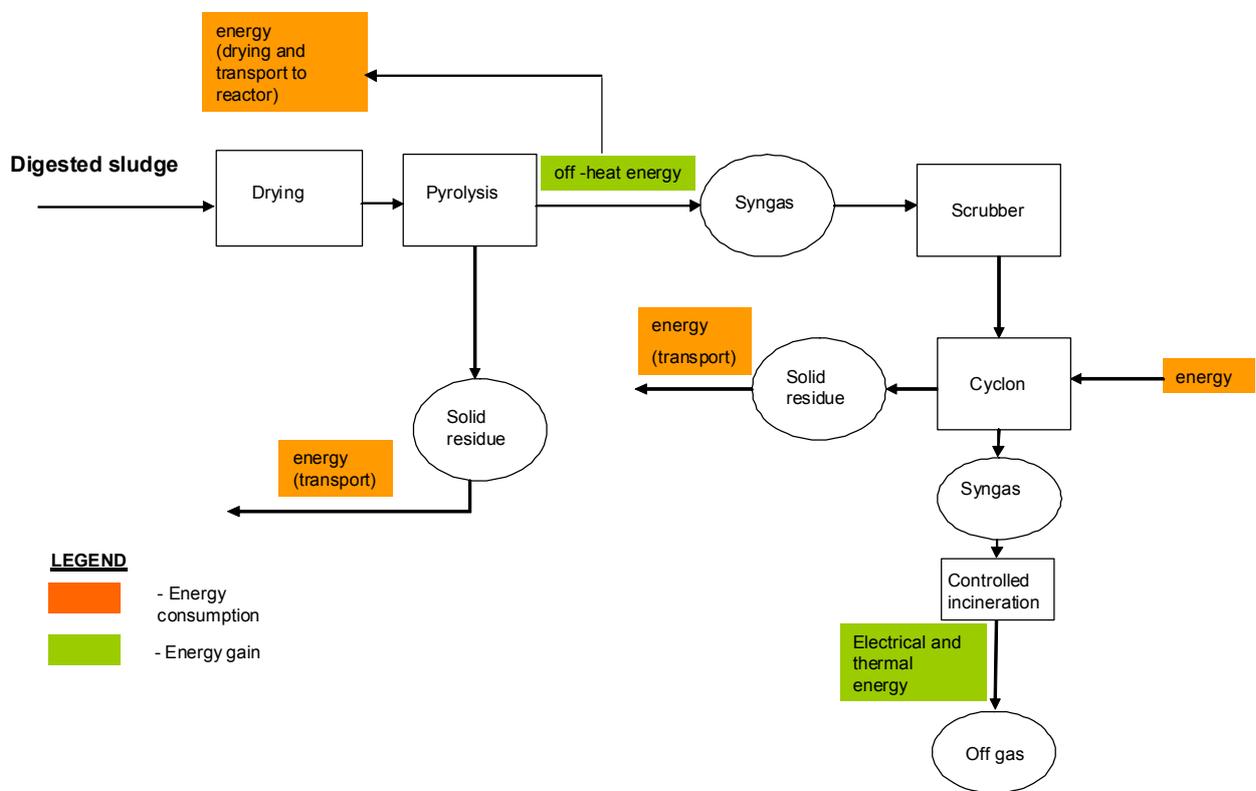


Figure 9 Schematic layout of the pyrolysis process

Major process characteristics could be found in the Neptune deliverable 2.1 and the short overview of the method is as follows: process is performed on temperatures higher than 1200°C, which allows for the production of clean gas free of tar. In addition, only solid residue is the additional outcome of the process, since the oily liquid phase is not created on such a high temperatures.

6.1 Contribution to sustainability

Obtained gas has the composition of syngas and consists of 85 percent CO and H₂ with smaller portion of CO₂ and CH₄. The heavy metals content of the solid residue is lower compared to the one of incineration ashes due to the increased volatilization into the process and the higher immobilization of the remaining heavy metals in the solid residue. This allows for safe disposal or further reuse of the material.

Phosphorus content of the solid residue of 6%-9% indicates the possibility of either recovering P by some of the already existing P recycling methods for incineration ashes or using solid residue direct as a fertilizer (this option is favored by the fact that heavy metals content is below the limits set for fertilizer, and at the same time questionable due to the low P bioavailability obtained during the lab tests).

Preliminary life cycle assessments on high temperature pyrolysis (HTP) indicate that the process might be environmentally more sustainable as compared to incineration assuming equal air emissions of heavy metals in both processes and recycling of copper during the demolition of the HTP plant. The main reason is a higher energy efficiency of HTP leading to surplus electricity production (640 kWh/ton dry matter), substituting electricity produced by fossil fuel and hereby lowering the global warming potential especially.

An additional advantage of HTP is the higher volatilization of heavy metals (which will be collected in gas scrubber) and therefore their lower concentration as well as better immobilization in the solid residue.

6.2 Limitations

The major emphasis concerning further improvements of the process is on creating gas with higher methane content so that the gas energetic value could be increased. In addition, under certain conditions the formation of polyaromated hydrocarbons (PAH) has been noticed and has to be eliminated.

6.3 Current state of application

An industrial size plant with a capacity of 25 t/d treating sludge has been operated for two years in Emmerich, Germany and one year in Neustadt, Germany. The purpose of these operations was long term testing of the reactor material and to gain industrial size operation

experience. Both plants have been dismantled and the first commercial plant is under construction in Eitting, Germany.

6.4 Costs

The costs could be presented as follows:

- Investment costs of a 25t/day unit with dryer, reuse of thermal heat for sludge drying and electrical energy production from syngas is approx. 9 million €. Energy is obtained in the form of syngas, which is 85 percent CO and H₂ with smaller portion of CO₂ and CH₄ and 50-60% of the energy content of natural gas. The calculation is done if the drier is fed with sludge at about 20-30% dry solids.
- Personnel costs are 200'000 €/year (4 people are required for operation and maintenance)
- Energy requirements are 400kWh/t of sludge but the process will produce 1200kWh/t of sludge (standard gas engine). The off heat energy from pyrolysis is used for sludge drying and therefore not included in the energy balance.
- Chemicals or any additives are not needed

7 Biopolymer Production from Biosolids

7.1 Bioplastic Production and Wastewater treatment

Bioplastics made from polyhydroxyalkanoate (PHA) biopolymers are recognised as outstanding candidates to replace conventional plastics. These bioplastics not only present industrially relevant mechanical properties but also are truly biodegradable. Furthermore, these biopolymers can be synthesized in mixed cultures, which have the capacity to utilise low-cost and renewable carbon sources, such as wastewater and biosolids.

Biosolids describe the sludge by-products produced by sewage treatment plants and constitute a burden for the operation of wastewater treatment plants since sludge handling and disposal represent a major operating cost. The research conducted under Neptune showcases the opportunity for the beneficial use of biosolids as a feedstock for the production of biopolymers. The production of PHA biopolymers is demonstrated in a reproducible fashion in laboratory-scale reactors fed with waste activated sludge (WAS) pretreated via high-pressure thermal hydrolysis (Figure 9). The process description and technology applicability have been previously outlined in Deliverable 2.1.

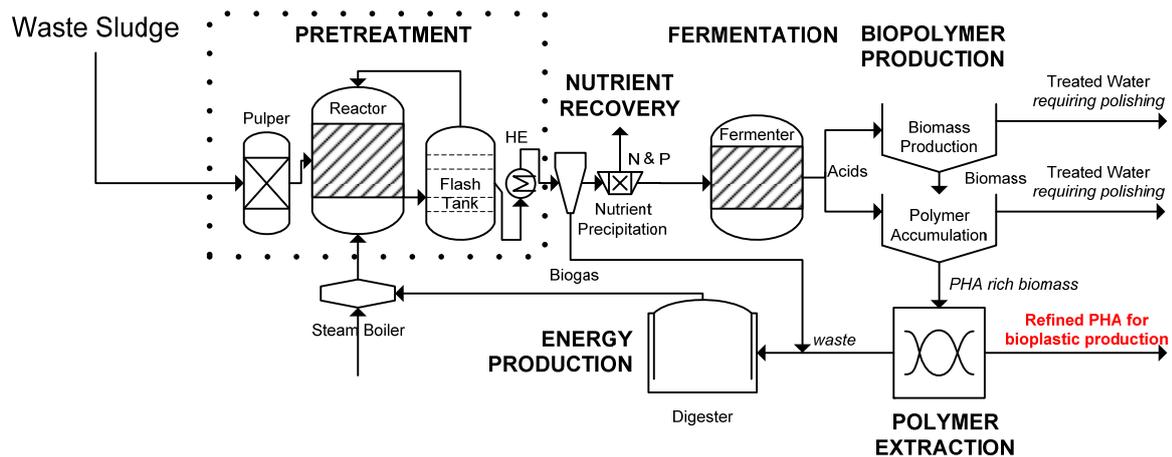


Figure 9 Process flow diagram used in the production of PHA bioplastic from pretreated waste sludge. The four main sub-processes are: sludge pretreatment, acidogenic fermentation, biopolymer production, and polymer extraction. Energy production and nutrient recovery could also be incorporated as anaerobic digestion of waste material and struvite precipitation, respectively.

7.2 Contribution to Sustainability

PHA production from waste biosolids and wastewaters contributes to global and local sustainable resource management. Life cycle assessment suggests that PHA production coupled to industrial wastewater treatment has merit from an environmental-impact perspective as well as an economic perspective compared to pure-culture PHA production and conventional waste management producing biogas (Gurieff and Lant, 2007). The benefits of coupling biopolymer production with wastewater management are largely due to the inherent characteristics of the feedstocks, products and by-products:

1. As evaluated here, PHAs can be produced by open, mixed bacterial cultures, thereby enabling the use of waste streams as feedstocks for PHA production. Waste streams invariably demand treatment/disposal, but as within Neptune's scope, they represent a renewable source of readily available carbon and nutrients. Biosolids can be utilized as a high volume, renewable resource yielding usable products, such as biopolymer, nutrients (nitrogen and phosphorus) and energy (Figure 9).
2. PHA biopolymers are completely biodegradable yet still possess thermoplastic properties comparable to those of petroleum-based polyolefins, such as polypropylene and polyethylene (Lee, 1996). Therefore, PHAs represent a promising sustainable alternative to conventional non-biodegradable petrochemical-based plastics.
3. Biogas, therefore energy, can be produced by anaerobic digestion of residual biomass generated as a by-product from biopolymer production. Biopolymer production might

even enhance the digestion of the residual biomass since processing for PHA extraction acts as pretreatment before digestion into biogas.

4. The production of biopolymers and energy (biogas) can be complemented with mineral recovery, i.e. N and P minerals, from side streams in agreement with a new concept of transforming wastewater treatment plants into biorefineries.

In addition, applying the biopolymer production technology in tandem with waste treatment may make for more sustainable conventional wastewater treatment processes. Waste organic carbon can be channeled towards the generation of biopolymers instead of being used for the growth of redundant biomass in need of further treatment. A potential outcome of biopolymer production during the wastewater treatment process is the reduction in waste sludge production, in aeration costs, and in nutrient requirements (Werker et al., 2007).

7.3 Technology Potentials and Challenges

Technology for biopolymer production in tandem with wastewater treatment is under current development. In the Neptune project, the focus was to utilize waste sludge pretreated with high-pressure thermal hydrolysis as a feedstock for PHA production, and the following aspects of the technology can be highlighted.

Feedstock: Sludge pretreatment yields a stream that is amenable to acidogenic fermentation. Specifically, waste activated sludge treated with high-pressure thermal hydrolysis is readily fermentable into a broad range of volatile fatty acids (VFAs) with at least 5 fold higher VFA production rates ($10\text{-}15 \text{ g COD}_{\text{VFA}} \text{ L}^{-1} \text{ d}^{-1}$) than WAS acidogenesis without pretreatment.

Product: PHA produced using pre-treated waste sludge as the feedstock consists of a copolymer of polyhydroxybutyrate and polyhydroxyvalerate ensured by the broad range of VFAs produced during acidogenic fermentation of the feedstock. The final PHA product has a flexible processing potential with broad application fields since it has a high molecular weight ($800\,000 \text{ g mol}^{-1}$), high thermal stability, and a hydroxyvalerate (3-HV) content of approximately 30%, which translates into low melting temperatures.

Process Challenges: The operation of the process with the inherent complexity of the fermented WAS stream pretreated via high-pressure thermal hydrolysis requires continued optimisation. For example, the recovery of high levels of nitrogen and phosphorus that may challenge PHA production can be evaluated. In the last months of the Neptune project, the feasibility of recovering P and N from such hydrolysed WAS stream as struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) has been demonstrated in a first experimental assessment (Karabegovic, 2009). Other pretreatment technologies yielding sludge solubilisation with less intensive

organic transformations and alternative process configurations including the wastewater treatment train can also be considered in order to reduce stream complexity.

7.4 Application

The economic feasibility of a PHA production process increases with an increase in the carbon strength of the waste stream (Gurieff and Lant, 2007). Therefore, this process would have higher application potential for sludge handling facilities with a large biosolids turnover (e.g., > 5000 tDS y⁻¹). As illustrated in Deliverable 2.1, for a flow of 6300 tDS y⁻¹ of WAS handled by the high-pressure thermal hydrolysis process (Cambi®) at the Oxley Creek Wastewater Treatment Plant (Brisbane, Australia), 85 t polymer y⁻¹ could be produced. A first economic evaluation of a PHA production process using open, mixed cultures and wastewater as feedstock was conducted by Gurieff and Lant (2007). A cost of approximately € 2 kg⁻¹ polymer (US\$ 3 kg⁻¹ polymer, 2005) led to an internal rate of return (IRR) of 20% for a specified feed strength of 20 g_{COD} L⁻¹ at a flow rate of 1 ML d⁻¹. Depending on the intended product use, i.e. PHA-containing biomass or refined PHA product, the downstream processing units for biomass pretreatment and polymer extraction need to be optimised; this however was outside the goals of this research work. Nevertheless, Gurieff and Lant's study indicated that the competitiveness of the PHA process resided in optimising energy consumption especially with respect to downstream processing, and that energy and trade waste policies can significantly impact the financial viability of the process.

REFERENCES

- Aguayo S, Munoz MJ, de la torre A, Roset J, de la Pena E, Carballo M (2004) Identification of organic compounds and ecotoxicological assessment of sewage treatment plants (STP) effluents. *Science of the Total Environment* 328 (1-3): 69-81.
- Foley J, Rozendal R, Hertle C, Lant P, Rabaey K (2009) A Life Cycle Assessment of Microbial Fuel Cells and Microbial Electrolysis Cells, *Submitted to Environmental Science and Technology*.
- Gurieff NB and Lant P (2007) Comparative Life Cycle Assessment and financial analysis of mixed culture polyhydroxyalkanoate production. *Bioresource Technology* 98, 3393-3403.
- Karabegovic L (2009) Nutrient recovery from anaerobically digested and hydrolysed waste activated sludge liquors by struvite precipitation. Master of Science Thesis. Department of Biotechnology. Lund University.
- Lee SY (1996) Bacterial polyhydroxyalkanoates. *Biochemical Engineering* 49, 1-14.
- Logan B, Hamelers B, Rozendal R, Schröder U, Keller K, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Microbial fuel cells: Methodology and technology, *Environmental Science and Technology* 40, 5181-5192.
- Rabaey K, Bützer S, Brown S, Keller J, Rozendal R (2009) Caustic soda production from synthetic and real wastewater using a lamellar bioelectrochemical system, *Submitted to Environmental Science and Technology*.
- Rozendal R, Hamelers H, Rabaey K, Keller J, Buisman C (2008) Towards practical implementation of bioelectrochemical wastewater treatment. *Trends in Biotechnology* 48 (8), 450-459.
- Werker A, Bengtsson S, Welander T (2007) Biopolymer production from biological waste treatment: activated sludge model evaluation of sludge production and nutrient mass balances for industrial wastewaters. *Proceedings of the 4th IWA Leading Edge Technologies. Singapore*.
- Zhang HC, Chen WR and Huang CH (2008) Kinetic modeling of oxidation of antibacterial agents by manganese oxide. *Environmental Science and Technology* 42(15): 5548-5554.