NEPTUNE

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

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CONTENTS

1 Introduction 3
2 COD removal and energy production: Microbial Fuel Cell 4
  2.1 MFC technology 4
  2.2 Sludge ‘revalorisation’ for current production in MFC 5
    2.2.1 Potential for MFC technology on the sludge line 5
    2.2.2 Description of work undertaken 6
    2.2.3 Results 6
  2.3 Pilot-plant operation on brewery wastewater 7
    2.3.1 Background 7
    2.3.2 Summary of results 8
    2.3.3 Outlook for MFC technology 9
  2.4 Added value products 9
  2.5 Cathode sustainablility 10
    2.5.1 Biocatalyzed cathode systems 10
    2.5.2 Iron chelated cathode systems 11
3 Micropollutant removal 13
  3.1 Ferrate 13
  3.2 Manganese Oxidation 15
    3.2.1 Production of Biogenic Manganese Oxides (BioMnOx) 15
    3.2.2 Chemical versus biogenic manganese oxides 16
    3.2.3 Application in a membrane reactor 17
    3.2.4 Perspectives 19
4 Sludge treatment and reuse 21
  4.1 Recovery of P and heavy metals: Sludge pyrolysis 24
    4.1.1 Process description 24
    4.1.2 Pilot plant trials and results 26
    4.1.3 Potential for phosphorus and heavy metals recovery 30
  4.2 Recovery of organics: Production of biopolymers from biosolids 32
    4.2.1 Background 32
    4.2.2 Potential areas of application 32
    4.2.3 Stage of development 33
    4.2.4 Technology description 33
    4.2.5 Process description 35

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 as a waste. These technologies comprise **microbial fuel cells** for energy recuperation, denitrification and production of added value product. For the removal of micropollutants two new technologies were developed. **Ferrate oxidation** can be used for the combined removal of pharmaceuticals and phosphate, and with **biogenic manganese oxides** it is possible to remove pharmaceuticals both chemically with manganese oxidation and biologically with manganese-oxidizing bacteria. Phosphor and heavy metal recovery with **pyrolysis** and **polymer production** from sewage sludge are two techniques developed for sludge revalorization.

This deliverable 2.1 **Novel technologies for wastewater and sludge treatment** describes the above mentioned technologies. With the new insight obtained during the Neptune project an up-to-date picture of these novel technologies could be provided.

In the deliverable 2.2 **New approaches for a sustainale WWTP design**, more information on the application in a wastewater treatment will be provided.

2 COD removal and energy production: Microbial Fuel Cell

2.1 MFC technology

Microbial fuel cells (MFCs) represent a new generation of wastewater treatment. While wastewater treatment was originally focused on nutrient removal, research nowadays focuses on finding combined solutions for wastewater treatment and energy/resource recovery. MFCs have recently gained considerable attention as they enable direct conversion of the chemical energy of electron donors, such as waste organics, into electrical energy (Rabaey and Verstraete, 2005). Briefly, they consist of an anode and a cathode (Figure 2.1). At the anode, micro-organisms oxidise the soluble organics present in a liquid feed stream, for example wastewater, and transfer the electrons to the anodic electrode. This transfer can either happen directly (Bond and Lovley, 2003; Gorby et al., 2006; Reguera et al., 2005) or indirectly via mediators (Rabaey et al., 2004). The electrons flow through an electrical circuit towards the cathode where a preferably high redox potential electron acceptor is reduced. To compensate for the electron flow through the electrical circuit, cations need to travel from anode to cathode through the bulk liquid and through the ion selective membrane separating anode and cathode. Overall, 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 e.g. produce hydrogen at the cathode. In this case, the reactor is called a Microbial Electrolysis Cell (Rozendal et al., 2008). A generic term for MFC and MEC is a Bio-Electrochemical System (BES) (Rabaey et al., 2007).

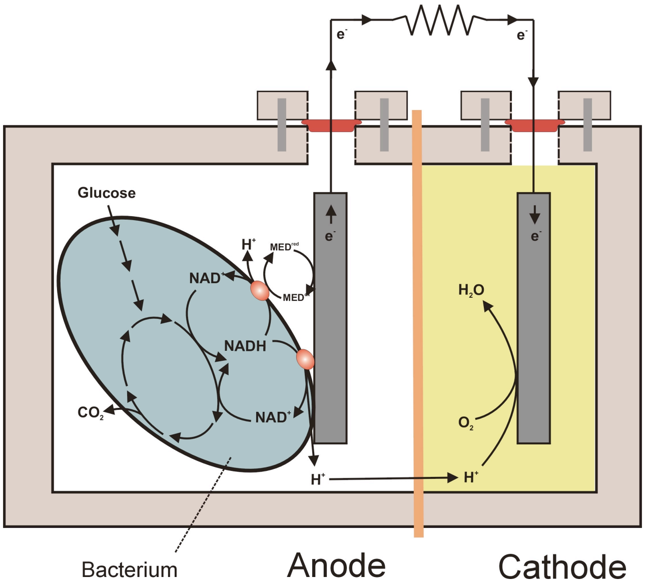


Figure 2.1 Schematic view of the anode and cathode of a microbial fuel cell (Rabaey and Verstraete, 2005)

2.2 Sludge ‘revalorisation’ for current production in MFC

2.2.1 Potential for MFC technology on the sludge line

Domestic wastewater treatment primarily runs through the activated sludge-based biological nutrient removal process. In this process, the sequential operation of aerobic, anoxic and anaerobic reactors allows the removal of organics, particulates and nutrients such as nitrogen and phosphorus compounds. The process is generally highly reliable, flexible towards scale and composition of the wastewater and very well described. However, the process has two major drawbacks: it is energy intensive and generates sludge. The removal of 1 kg of COD gives rise to the formation of about 0.4 kg of sludge (Weemaes and Verstraete, 2001). Settling at the end of the process generally separates this sludge, and part of it is disposed. Prior to disposal, the sludge is concentrated to limit its volume, via thickeners, belt presses or centrifuges, all these processes being energy intensive. Additionally, the final disposal of the sludge poses issues in regions where it cannot be brought onto agricultural soil. The overall cost of disposal via incineration, for example, amounts to about $900 per tonne dry weight (Weemaes and Verstraete, 2001).

To recover part of the energy contained in the sludge and simultaneously decrease the sludge volume to be disposed, anaerobic digestion has been proposed as a valuable candidate. A significant fraction of the sludge can be converted in digesters, creating valuable methane gas that is generally combusted on site for heat or electricity generation. Secondary sludge from domestic treatment is generally only partially usable for digestion. To improve the process at a treatment plant near Brisbane, a CAMBI system (100-180ºC, 6 bar, HRT ~30min) that generates a waste stream that is amenable to high rate acidogenic fermentation and the production of volatile fatty acids (VFAs) was installed (Picworth et al., 2006).

Directly feeding sludge into a MFC appears not advisable, as the viscous nature of the sludge would cause limited diffusion of the organics to the electrode surface, and of ions between anode and cathode. Therefore, the CAMBI liquefied and subsequently pre-fermented sludge may be a more suitable stream, as it will be highly enriched in VFA. Past experience with MFCs has indicated that the latter, such as acetate (Rabaey et al., 2005), propionate (Bond and Lovley, 2005) and butyrate (Liu et al., 2005a) are well suited as carbon sources for current generation.

2.2.2 Description of work undertaken

The main focus of the work was to investigate the potential of using VFA mixtures, as present in fermented sludge hydrolysate, for current generation using microbial fuel cells. The proposed process diagram is show in (Figure 2.2). The work has comprised of two parts:

Part One: analysis of MFC performance with synthetic influent (single and mixed VFA), evaluating the impact of loading and anode potential on both performance (i.e. current generation) and VFA removal;

Part Two: analysis of MFC performance with fermented sludge hydrolysate.

The work thus far has been undertaken with a granular-type frame reactor with potassium ferricyanide as the catholyte.

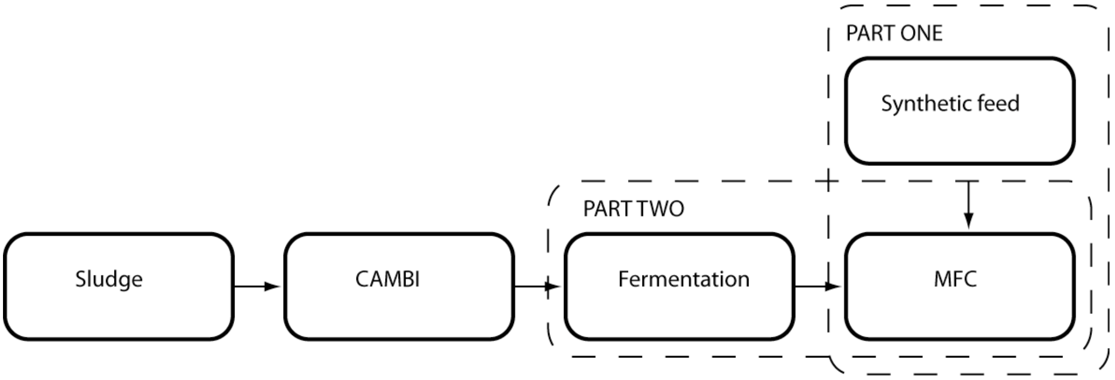


Figure 2.2 Flow diagram of concept

2.2.3 Results

The work thus far with pure VFA influent streams has demonstrated that the main constituents of fermented sludge hydrolysate can effectively be degraded using a MFC (loading of 1.9 gCOD/L.d, 500 mg/L COD). However, large differences exist between the VFAs, with acetate and propionate more readily used. This highlights the possible role of a fermenter operating in tandem, producing an MFC influent with a higher concentration of the VFAs that are more readily degradable. Further work with potentiostatic control of the MFC reactors (i.e. no longer limited by constant resistance between the positive and negative poles of the cell) will help identify the operational parameters necessary to achieve a high Coulombic efficiency with the whole VFA spectrum.

Initial work with mixed synthetic influent streams, representing the typical output of a fermenter operating with CAMBI effluent, have demonstrated the ability of the MFC technology to produce a steady current over a reasonable time period (two weeks), with the removal of VFAs [over 50% reduction of COD (mgCOD/L)] and achieving Coulombic efficiencies of approximately 50%. Preliminary tests with ethanol as the influent have shown that it can also be effectively degraded in MFCs, achieving Coulombic efficiencies of between 60 - 90%. Further work with potentiostatic control will assist in identifying the optimal operating conditions with the synthetic mixed stream. In addition, further work with reactor design (with a focus on improving flow distribution, current collection and electrode material) will assist in improving the process. Initial experiments using fermented CAMBI effluent as the influent into a granular bed frame-type MFC have highlighted the issues of a high solids concentration. Centrifuging and subsequent dilution of the influent to the fermenter in future work is expected to improve the quality of the influent to the MFC, hence achieving more than the 2% Coulombic efficiency observed in preliminary measurements.

Analysis of granules harvested from both pure and mixed synthetic reactors with PCR-DGGE and Pareto-Lorenz curves (Marzorati et al. 2009) has demonstrated that different communities correlate with the conversion of different VFA. More specifically, clusters for acetic and hexanoic acid *(Geobacter* sp., *Comamonas* sp. and *Pelobacter* sp.) differed from propionic and butyric acid (*Pseudomonas, Bacillus* and *Microbacterium* species). Pareto-Lorenz curves indicated that diversity could be the key for higher MFC performance.

2.3 Pilot-plant operation on brewery wastewater

2.3.1 Background

MFC research up till now has focused on laboratory scale reactors. At lab-scale, the process is rather straightforward to control and synthetic influents are generally used. But, the main issue is that a vast difference exists between lab and pilot scale MFCs. This difference is mainly caused by the electrochemical nature of the process, in relation to a number of requirements for wastewater engineering.

Two reactor designs were developed (tubular and rectangular), however, the tubular reactor design was commissioned since the manufacturing of the rectangular design seemed to be more complicated and more expensive. The performance of different electrode materials was investigated in the laboratory to finally confirm the carbon brush electrode as the most suitable material. The experience of the construction for a single module was gained in the AWMC laboratory through a model size reactor of 13L volume. The research into optimisation of the hydraulics and the electrical circuitry was part of the pilot plant operation.

In September 2007, 11 reactors of 100 L volume were started up. All of the reactor modules were constructed with the carbon brushes on the anode and the cathode. Each 6 reactors on one sump side were recirculated with a magnetic drive pump and fed with a peristaltic pump.

A shed with all control devices was located next to the sump and the reactor modules. Reactor 12 was only started up at the beginning of February 2008. Target performance indicators can be found in (Table 2.1).

2.3.2 Summary of results

The application of the MFC pilot plant in a real world context revealed many challenges of an operational, hydraulic, electrical, microbiological and constructional nature. However, the modular design of the pilot plant enabled parallel investigation of many of those challenges and different parameters. The main operational challenge was the concentration fluctuation and composition of the real wastewater that was supplied to the pilot plant. To solve this issue, the brewery wastewater was filled batch wise in a big feed tank of a volume of 5000L. The clogging caused by the solids of the wastewater could be addressed by including a settlement zone in the same feed tank.

Table 2.1 Summary of pilot scale results

Parameter	Value target	Value achieved
Power output (maximal)	50W	0.8W (2A @ 0.4V)
Power density		0.5 W m^{-2} (membrane area) 8.5 W m^{-3} (reactor volume)
COD removal rate	5 kg COD m^{-3} d^{-1}	0.2 kg COD m^{-3} d^{-1}
COD removal %	>90%	15%
Coulombic efficiency	>80%	5%
Voltage	500 mV per module	400 mV
Anode potential	-200 to +500 mV vs. NHE	-220 mV vs. NHE
Cathode potential	+200 to +500 mV vs. NHE	+200 mV vs. NHE
Influent COD concentration	5000 mg L^{-1}	3200mg L^{-1}
Flow rate	0.4 – 6 m^3 d^{-1}	0.08 m^3 d^{-1} $reactor^{-1}$ 1 m^3 d^{-1} $12reactor^{-1}$
Recirculation flow rate	2-144 m^3 d^{-1}	0.4 m^3 d^{-1} $reactor^{-1}$ 5 m^3 d^{-1} $12reactor^{-1}$
Organic loading rate	2-10 kg COD m^{-3} d^{-1}	1 – 2.5 kg COD m^{-3} d^{-1}
Influent pH	4.8	4.8
Number of modules	24	12
Volume of each module	96 L	96 L
Total reactor volume (anode only)	1152 L	1152 L
Volume of sump (for 12 reactors)	360 L	360 L
Total pilot plant volume (including sumps)	1375 L	1375 L

The maximum performance that was achieved of the pilot plant was about 8 W per m^3 reactor volume (corresponds to 2 A @ 0.4 V per module). This is notably lower than the initial target (see Table 2.1); this low performance level had several origins. Firstly, the conductivity of the used wastewater was low. Secondly, several issues with the site plant affected the wastewater inflow to the pilot – several management practice changes required modifications to the pilot. Thirdly, addressing the clogging of feed structures was a complex undertaking, which caused issues over more than half the operation time of the pilot. Fourthly, operating an air cathode is feasible – but due to the variability in the anode performance we were not able to optimise the cathode within the timeframe of this project. Finally, intrinsically the design had a suboptimal volume/surface ratio and current collection. The operation of the pilot plant has resulted in many important – even crucial - insights with respect to operation and control of upscale MFCs that would not have been discovered under laboratory conditions.

2.3.3 Outlook for MFC technology

There is a clear understanding of what limited the performance at pilot-scale and how the design should be modified. An improved version of the pilot is now tested at lab scale, and is already performing close to the target of 1000 A m^{-3} at litre scale and using low conductivity synthetic feed. However, the scope of this system has moved away from energy generation. The most important point to be made is that based on the inherent complexity of the MFC systems, MFC technology will probably not become a true alternative technology to anaerobic digestion for production of power from wastewater treatment. However, when the target is shifted from electricity production to the production of valuable chemicals at the cathode of the *same* system, we see a paradigm shift for wastewater treatment. In addition, a life-cycle analysis confirmed that Bio-Electrochemical Systems represent a clear benefit to the environment, mainly due to a decrease in greenhouse gas emissions.

2.4 Added value products

Besides the production of electrical power with MFCs, recently, more emphasis is being given to added value purposes for Bio-Electrical Systems (BESs), such as the production of gaseous energy carriers (H_2, CH_4) (Clauwert and Verstraete, 2009; Liu et al. 2005b; Rozendal et al., 2006), water purification (nitrate, phosphate, calcium, sulfide, perchlorate and chlorinated solvents removal) (Clauwaert et al. 2007a, Rabaey et al., 2005) and the use of BESs as biosensors (Kim et al., 2003). Also the production of chemicals like ethanol, polyhydroxyalkanoates, and hydrogen peroxide might enhance the economical feasibility of BESs.

Hydrogen peroxide can be chemically produced at the cathode of a BES by the two electron reduction of oxygen. In MFCs with a carbon and graphite electrodes, a hydrogen peroxide concentration up to 100 mg H_2O_2 L^{-1} can be obtained (see Figure 2.3). This hydrogen peroxide could be used as an oxidant for micropollutant removal in the presence of a catalyst. For example, 25 mg L^{-1} 3-chloroaniline could be oxidized by hydrogen peroxide in the presence of iron (Fe^0) and platinum.

2.5 Cathode sustainablility

Since the use of unmodified carbon or graphite-based cathodes is associated with higher overpotentials for oxygen or proton reduction, the use of a catalyst is generally required in BESs. Platinum is considered to be the benchmark catalyst in BESs. Despite its good reduction properties, several disadvantages are associated with the use of platinum in BESs (cost, environmental unfriendly production, poisoning). Therefore, new cathode systems are required to make BESs more sustainable and economically viable. Two new cathode systems were developed: 1) biocatalyzed cathode systems and 2) iron chelated cathode systems.

2.5.1 Biocatalyzed cathode systems

Up till now, most BESs consisted of a biocatalyzed anode combined with an abiotic cathode. Recently, there has been an increasing interest in replacing abiotic cathodes for biocathodes in which enzymes enhance the reduction catalysis (He and Angenent, 2006).

Nitrate reducing biocathodes could be developed with an enhanced denitrification activity in the anode up to 0.5 kg NO_3^--N m^{-3} NCC d^{-1} (NCC: net cathodic compartement) while oxidizing acetate in the bioanode (Clauwaert et al., *submitted*). Also, oxygen reducing biocathodes were developed that demonstrated a competitive current (275 A m^{-3} MFC) and power density (110 W m^{-3} MFC) compared to MFCs with platinum containing cathodes (Clauwaert et al., 2007b).

The crucial parameters in developing highly performing biocathodes were the selection of the appropriate inoculum, external resistance, cathode potential, cell voltage and pH. It was found that the start-up of an open air biocathode could be accelerated by the presence of chemically oxidized manganese oxides on the cathode. Biomineralized manganese oxides have been used for an enhanced oxygen reduction by *Leptothrix discophora* where manganese served as electron shuttle between the cathode and the microorganisms (Rhoads et al., 2005). However, no enhanced biocathode activity was obtained in the presence of manganese oxides. Manganese oxides are known for decomposing hydrogen peroxide (Hasan et al., 1999) and it might be that chemically produced hydrogen peroxide prolonged the start-up of aerobic biocathodes.

In Figure 2.3, the start-up of a biocathode with an external resistor of 500 Ω is visualized, together with the peroxide concentration in the cathode electrolyte. The peroxide concentration first increases and later decreases, as the biocathode becomes active and the cathode potential increases. It can be that an increased catalase activity protects the developing biocathodic community or that the biologically induced increase in cathode potential makes peroxide production thermodynamically unfavorable.

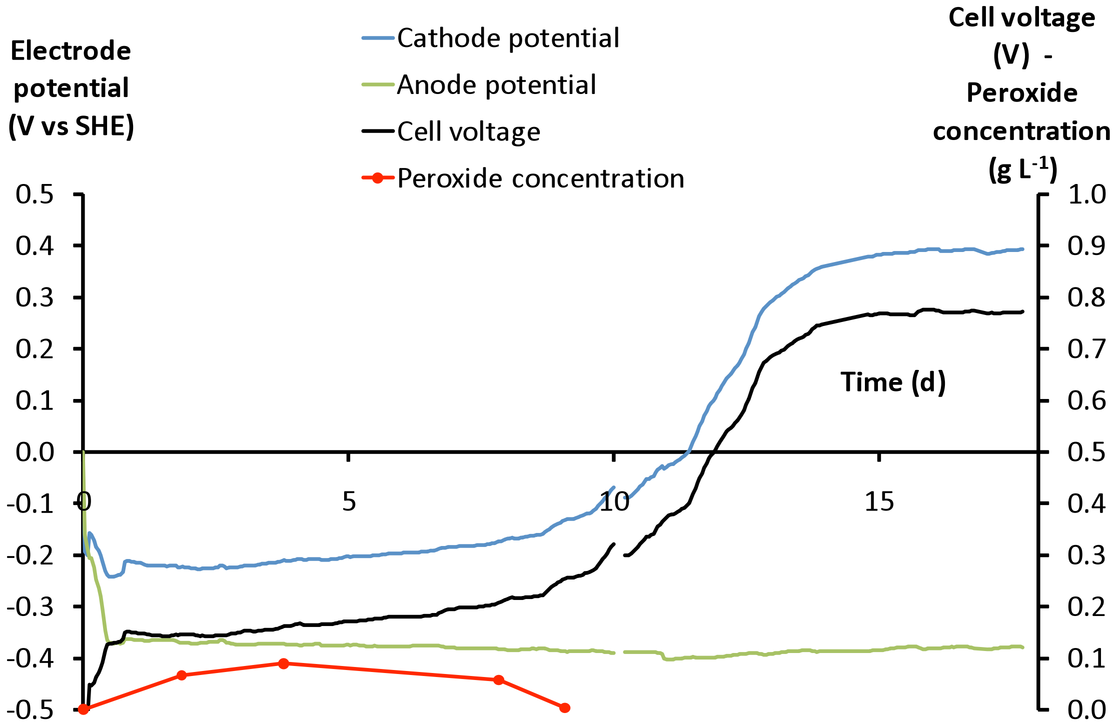


Figure 2.3 The evolution of the cell voltage, the anode and cathode potential and the hydrogen peroxide concentration during the start-up of a MFC with an open air biocathode with an external resistor of 500 Ω.

2.5.2 Iron chelated cathode systems

The use of various iron chelating molecules to operate MFCs with an iron based chelated catholyte was investigated. The poor solubility of ferrous and ferric iron at a pH above 2.5 hampers the use of this redox couple as a catholyte in MFCs. By administering iron chelating molecules (EDTA, NTA, citrate and succinate), the solubility of the ferric/ferrous couple can be significantly increased even at a neutral pH. In case of the Fe-EDTA catholyte system, a stable current generation of over 8 days was attained. During this period, the cumulative charge production exceeded the single oxidation capacity of the catholyte by a factor 5. Two reference systems were tested: a hexacyanoferrate (HCF) cathode and a plain graphite cathode operated with a buffer solution. The HCF system outcompeted all the other systems tested both in terms of current generation and power production (Table 2.2), but it needed a regular replacement. Nevertheless, the Fe-EDTA catholyte generated a comparable maximum current and continuous current as the HCF system, but the power generation and open current voltage (OCV) were respectively 50 and 30 % lower (Table 2.2).

Table 2.2 Overview of the equilibrium potential of the solution (Eh) and parameters during the operation of the MFC with these catholytes. The reported parameters are: pH (start and end), maximum open circuit potential (OCV_{max}), continuous current generation at 25 Ω ($I_{25\Omega}$) (3.9 $m\Omega.m^3$), maximum current generation (I_{max}) and volumetric power generation ($P_{v,max}$) during polarization.

Cathode system	Eh[1]	pH		OCV_{max}	$I_{25\Omega}$	I_{max}	$P_{v,max}$
	mV	*start*	*end*	*mV*	*mA*	*mA*	*W.m^{-3}TAC*
Fe-EDTA	440	3.4	9.5	457	10.4 ± 4.0	34.4 ± 4.3	22.9 ± 10.6
Fe-NTA	479	3.8	9.0	454	6.7 ± 3.0	25.6 ± 3.4	9.9 ± 2.8
Fe-Citrate	466	1.9	8.5	452	7.3 ± 3.5	7.8 ± 1.8	2.9 ± 0.8
Fe-Succinate	661	1.6	9.3	874	2.2 ± 1.0	9.0 ± 2.8	4.4 ± 1.8
Hexacyanoferrate	384	7.0	7.0	655	12.1 ± 3.1	35.4 ± 7.2	47.1 ± 17.3
Plain graphite	n.a.	7.0	9.3	256	3.8 ± 1.4	20.8 ± 3.0	5.8 ± 1.3

[1] : expressed versus Standard Hydrogen Electrode (SHE)

n.a. : not applicable

3 Micropollutant removal

Pharmaceuticals, personal care products, antiseptic products, and many household and industrial chemicals are often recalcitrant and not sufficiently removed in conventional wastewater treatment. These compounds enter the environment through wastewater effluent discharges and are a potential threat to aquatic life. Ozonation is a promising technique for micropollutant removal (see WP1). In this section, two novel technologies ferrate and manganese oxidation are described.

3.1 Ferrate

The ferrate (Fe(VI)) application in municipal wastewater treatment is a novel process for simultaneous phosphate removal and micropollutant oxidation (Figure 3.1).

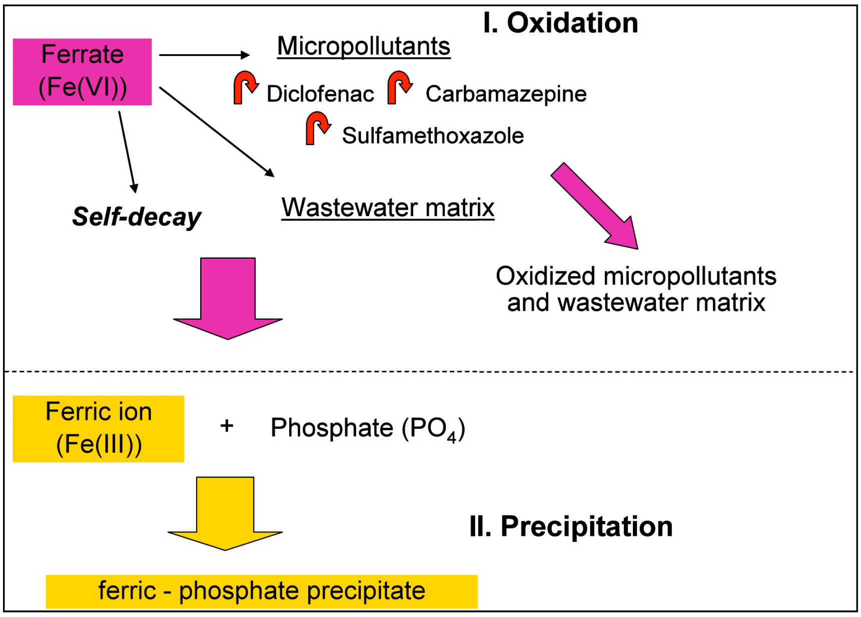

I. Oxidation
Ferrate (Fe(VI))
Micropollutants
Diclofenac
Carbamazepine
Sulfamethoxazole
Self-decay
Wastewater matrix
Oxidized micropollutants and wastewater matrix
Ferric ion (Fe(III))
+
Phosphate (PO_4)
II. Precipitation
ferric - phosphate precipitate

Figure 3.1 Schematic view of ferrate application in municipal wastewater treatment

Ferrate (Fe(VI)) is a potential water treatment chemical that's unique feature is its dual function as an oxidant and a subsequent coagulant as ferric hydroxide. Within the Neptune project, the ability of (Fe(VI)) to oxidize a broad range of micropollutants was studied (

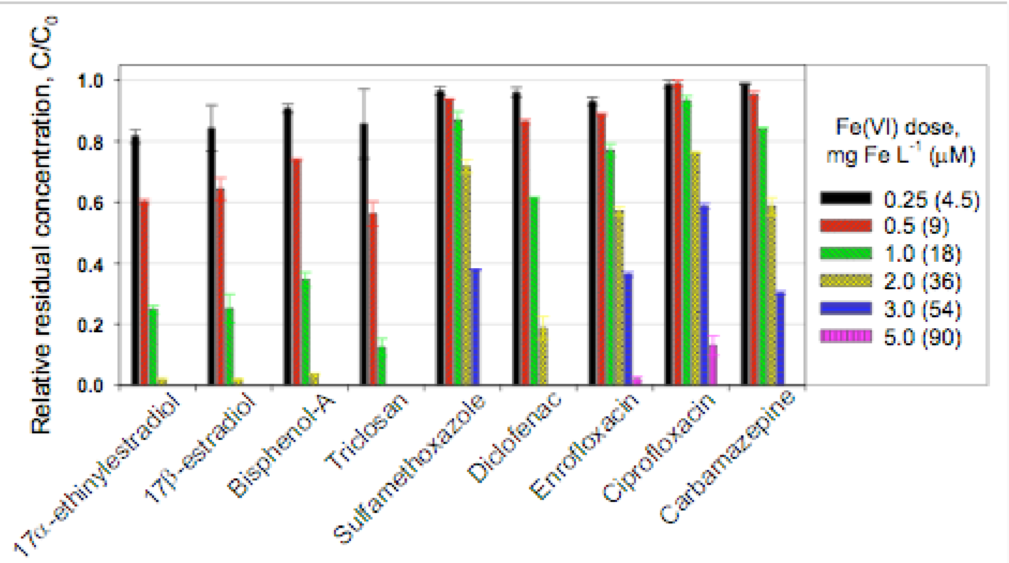


Figure 3.2 Oxidative elimination of selected micropollutants during treatment of a secondary wastewater effluent as a function of the Fe(VI) dose (0.25 –5.0 mg Fe L^{-1}). Experimental conditions: [micropollutants]$_0$ = 0.1 – 1 μM, [PO$_4$]$_0$ = 3.5 mg P L^{-1}, [DOC] = 5.1 mg C L^{-1}, pH = 7 and T = 23±2 °C.

In addition, the combined process of micropollutants elimination and phosphate removal (Figure 3.3) was investigated. It could be shown that Fe(VI) doses needed to eliminate micropollutants containing electron rich moieties (5 mg Fe L^{-1}) are lower than those needed to reduce phosphate concentrations from 3.5 to 0.2 mg P L^{-1} (> 8 mg Fe L^{-1}). Hence, the combined use of (Fe(VI)) and the less expensive Fe(III) could be of economic interest. The comparison of different forms of iron (Fe(VI), Fe(III), Fe(II)) revealed that Fe(VI) is as efficient as Fe(III) in terms of phosphate removal (Figure 3.3a).

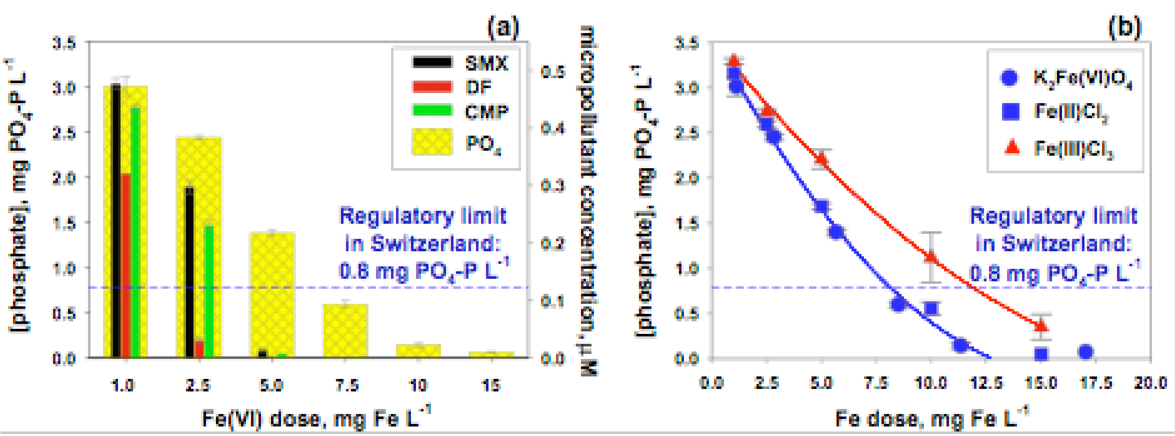
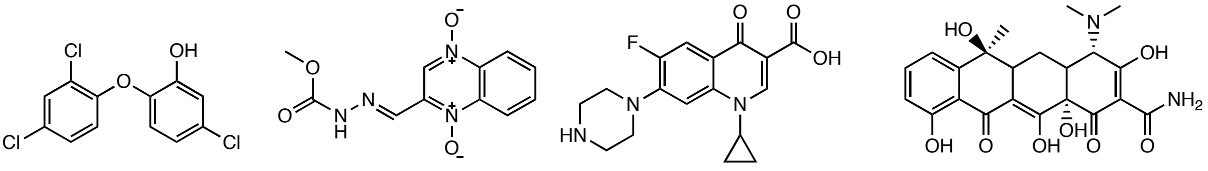


Figure 3.3 (a) Oxidative elimination of selected micropollutants and subsequent removal of phosphate during treatment of secondary wastewater effluent as a function of the Fe(VI) dose (1.0 – 15 mg Fe L^{-1}) and (b) Comparison of phosphate removal efficiency for various forms of iron. Experimental conditions: [micropollutants]$_0$ = 0.5 – 1 μM, [PO$_4$]$_0$ = 3.5 mg P L^{-1}, [DOC] = 5.1 mg C L^{-1}, pH = 7 and T = 23±2 °C.

Ozone is another feasible oxidant for enhanced wastewater treatment. Hence, its ability to oxidize micropollutants was compared to that of (Fe(VI)) in the same wastewater matrix. The results showed that for similar oxidant doses, (Fe(VI)) is as efficient as or slightly less efficient than ozone with (Fe(VI)) having the benefit of phosphate removal. Therefore, we propose (Fe(VI)) application in municipal secondary effluent wastewater in combination with flocculation filtration as a powerful tool to lower the micropollutants loads to the aquatic environment and at the same time, control phosphate concentrations to meet legal requirements. The addition of ferrate directly to the activated sludge system reduced the efficiency to about 3% compared to effluent treatment due to the strong interaction of ferrate with the activated sludge.

3.2 Manganese Oxidation

Manganese oxide is a widespread oxidant in soils, sediment and marine environments and it can oxidize different types of substances (Figure 3.4), including antibacterials and related compounds with phenolic and fluoroquinolonic moieties, aromatic N-oxides, tetracyclines and estrogenic compounds such as the synthetic hormone 17α-ethinylestradiol (Sabirova et al., 2008; Zhang et al., 2008). In the Neptune project, biologically produced manganese oxides were investigated for their oxidizing capacity towards micropollutants in wastewater. The reactivity of biologically and chemically produced MnO_2 was compared and biogenic manganese oxides were tested in a continuous reactor setup for the removal of recalcitrant pharmaceuticals in wastewater effluent.



Triclosan

Carbadox

Ciprofloxacin

Tetracycline

Figure 3.4 Examples of structures of a phenolic compound (triclosan), an aromatic N-oxide (carbadox), a fluoroquinolonic compound (ciprofloxacin) and tetracycline

3.2.1 Production of Biogenic Manganese Oxides (BioMnOx)

Manganese ions (Mn^{2+}) can be oxidized to MnO_2 by manganese-oxidizing bacteria (MOB) such as *Pseudomonas* or *Leptothrix* species. *Pseudomonas putida* is a heterotrophic bacteria, easy to cultivate on glucose as a carbon source. *P. putida* rapidly oxidize Mn^{2+} and the biologically oxidized manganese precipitates as MnO_2 on the cell wall of the bacteria. The combination of the active bacteria *P. putida* with MnO_2 is called BioMnOx (Figure 3.5).

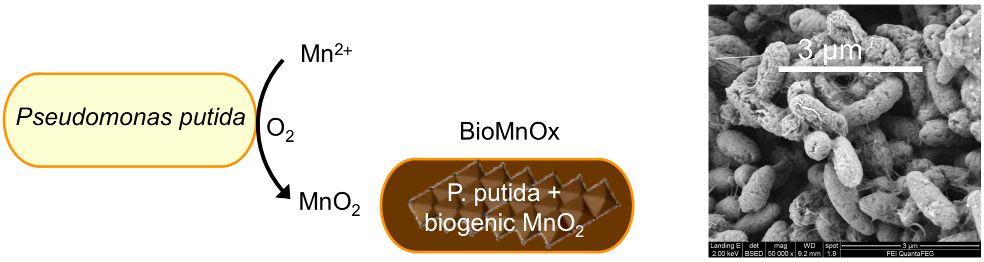


Figure 3.5 Formation of BioMnOx and SEM picture of clustered BioMnOx

3.2.2 Chemical versus biogenic manganese oxides

For the application of chemical MnO_2, an acidic environment (pH 4-5) is required to enhance the removal efficiency. According to the reduction half reaction (1), solid manganese dioxide is reduced to soluble Mn^{2+}, which subsequently inhibits the overall reaction. The latter effect is more pronounced at neutral pH.

$$MnO_2(s) + 4\ H^+ + 2\ e^- \rightarrow Mn^{2+}(aq) + 2\ H_2O \qquad (1)$$

The main advantage of biogenic manganese oxides (BioMnOx) over chemical MnO_2 is the ability of the bacteria to re-oxidize these soluble reduced manganese species, thus removing the inhibiting effect on the process. In this way, there is no need for an extensive acidification and the chemical catalyst is regenerated. In Figure 3.6 the re-oxidation of the reduced manganese and the ability of the manganese oxidizing bacteria to further remove the biodegradable oxidation products formed, are illustrated.

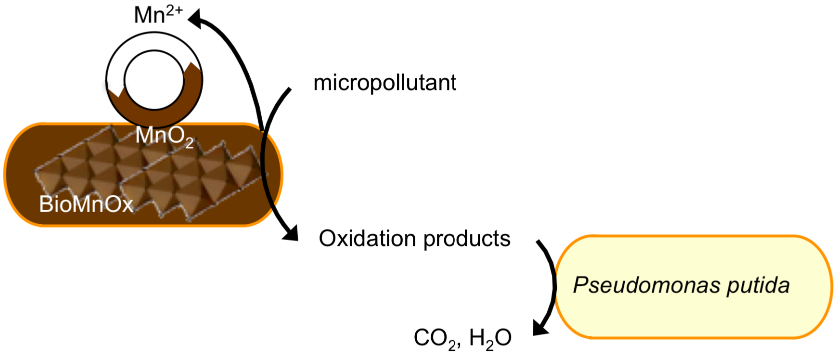


Figure 3.6 Oxidation action of biogenic manganese oxide on micropollutants, re-oxidation of reduced manganese species and biodegradation of oxidation products

AT acidic pH, the performance of biogenic manganese oxides is comparable to chemical MnO_2 because below pH 6.5, no bacterial manganese re-oxidation occurs (Boogerd and de Vrind, 1987). At neutral pH, biogenic manganese oxides are 10 times more reactive than chemical MnO_2. This is illustrated in Figure 3.7 with the pharmaceutical compound diclofenac, a steroidal anti-inflammatory and analgesic drug widely spread in wastewater effluent in Europe.

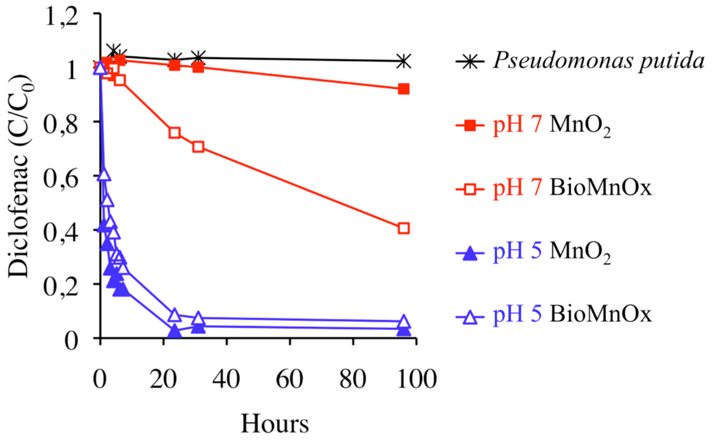


Figure 3.7 Diclofenac removal with chemical MnO_2 (4.6 mg Mn L^{-1}) and BioMnOx (3.5 mg Mn L^{-1}) at pH 4.7 and 7.0. C_0 is 3.87±0.21 mg L^{-1} and BioMnOx. Control is a Mn-free *Pseudomonas putida* culture at pH 7.0.

3.2.3 Application in a membrane reactor

For the application of BioMnOx for micropollutants removal from wastewater effluent in a lab scale membrane bioreactor (MBR) of 0.2 L (Figure 3.8), it was important to monitor the pH and adjust it if necessary because the removal efficiency could be 6-fold increased. The pH was therefore maintained at 6.5.

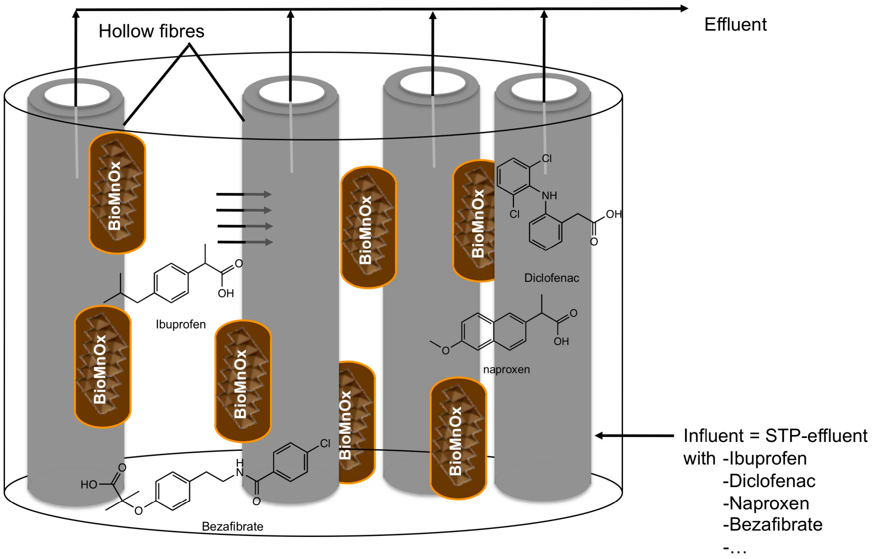

Hollow fibres
Effluent
BioMnOx
Ibuprofen
OH
O
Cl
NH
Cl
OH
O
Diclofenac
naproxen
O
OH
HO
Cl
H
N
Bezafibrate
Influent = STP-effluent
with -Ibuprofen
-Diclofenac
-Naproxen
-Bezafibrate
-…

Figure 3.8 Scheme of a membrane bioreactor with BioMnOx for polishing of wastewater effluent

To provide sufficient mixing, a recycle was applied over the outer compartment containing the BioMnOx. Aeration was applied to saturate the recycle fluid with oxygen (8 mg O_2 L^{-1}) because the presence of oxygen is required for the bacterial re-oxidation of reduced Mn species. Aeration can also be provided directly in the reactor. Because of the densely packed hollow fibers, BioMnOx was in close contact with the membrane surface and retained physically in the reactor. However, in a conventional MBR, BioMnOx would be mainly present as suspended matter, which would increase mixing and therefore reactivity.

The main factors influencing the oxidation of micropollutants with BioMnOx are the complex matrix of wastewater effluent, including residual organics and ions such as NH_4^+, the “aging” of the BioMnOx and the presence of other micropollutants. Matrix-effect tests showed a decreased diclofenac removal by a factor of 2 at a stable pH of 6.8 and by a factor of 5 in the absence of a pH buffer. After 1.5 months without C-source, BioMnOx showed a 1.5-fold lower activity towards diclofenac removal.

The reactor was operated for a period of 45 days on wastewater effluent, retrieved from a municipal wastewater treatment plant. Different hydraulic residence times (HRT) were applied as shown in Figure 3.9.

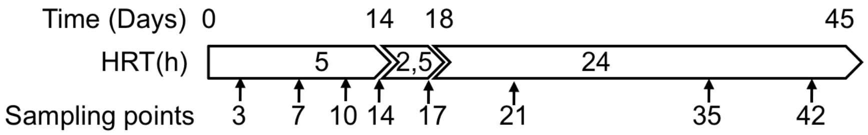


Figure 3.9 Operation of MBR with BioMnOx for the removal of micropollutants from wastewater effluent: HRT and sampling points.

Influent and effluent samples, taken twice a week, were analyzed for the presence of 35 compounds and 24 were detected frequently. The influent concentrations were below 1 µg L^{-1} except for the iodinated contrast media (ICM). For example diclofenac was detected between 200 and 800 ng L^{-1}. Figure 3.10 shows the removal efficiencies for all the compounds detected. The acidic pharmaceuticals ibuprofen, diclofenac, naproxen and benzafibrate, the antibiotic clarithromycin and the analgesic codeine are removed by BioMnOx in a MBR. In Figure 3.11, the influence of HRT on the removal of acidic pharmaceuticals is presented. Diclofenac removal at ng L^{-1} levels is sensitive to the HRT applied.

Diclofenac removal drops significantly when HRT is lowered from 5 to 2.5 h and it is subsequently restored when HRT is raised to 24 hours. After 3 weeks, removal of ibuprofen is hampered. It is likely that ibuprofen is biologically degraded by the manganese-oxidizing bacteria *Pseudomonas putida*, that is part of the BioMnOx, because ibuprofen is biodegradable (Joss et al., 2006). After 3 weeks of starvation, the biological action of BioMnOx (removal of biologically degradable matter and re-oxidation of Mn^{2+}) is decreased. Nevertheless, Mn^{2+} concentrations were below detection limit (0.1 mg L^{-1}).

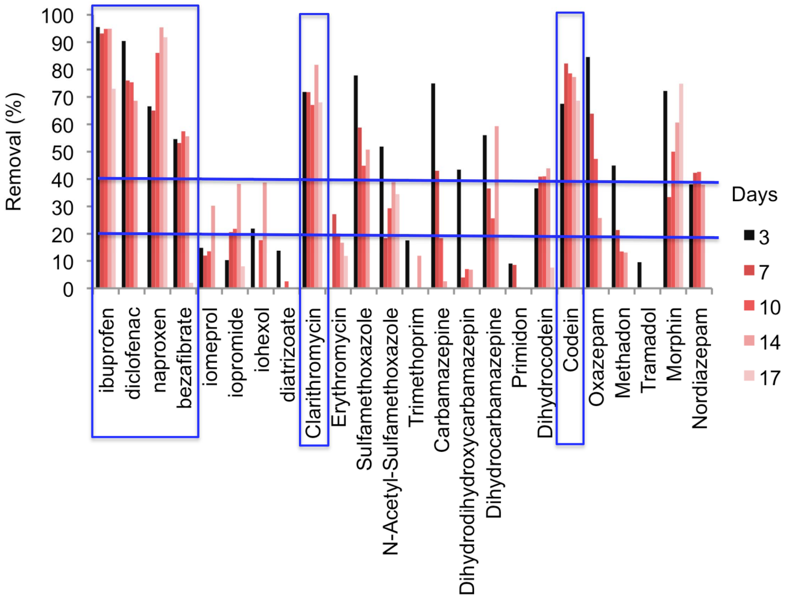


Figure 3.10 Removal efficiency of 24 pharmaceutical compounds detected in wastewater effluent in a MBR with BioMnOx. Boxes indicate the compounds removed for more than 40%.

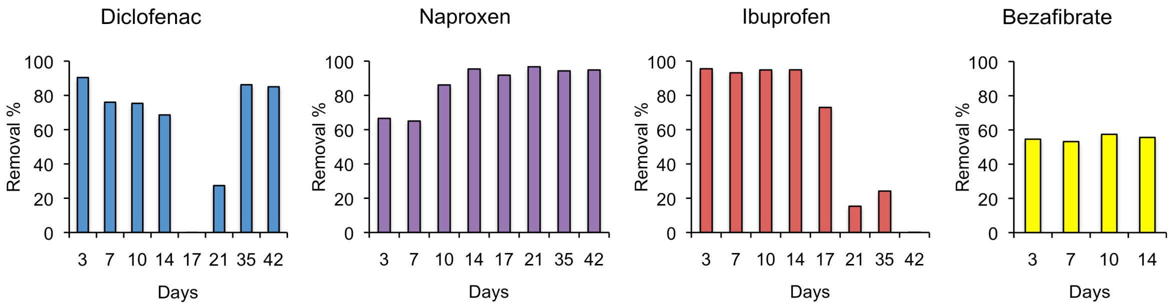


Figure 3.11 Removal efficiency of 4 acidic pharmaceuticals detected in wastewater effluent in a MBR with BioMnOx. Bezafibrate (22 ng L^{-1}) was only present during the first 2 weeks, and it was removed below detection limit (10 ng L^{-1})

3.2.4 Perspectives

We demonstrated the effective removal of the acidic pharmaceuticals (diclofenac, naproxen and bezafibrate) with biologically produced manganese oxides for at least a standing period of 1.5 months. Due to BioMnOx exhausting under starvation conditions, biological degradation of ibuprofen is hampered after a period of 3 weeks. To keep the biological activity of the BioMnOx optimal, a C-source should be provided. Future tests with raw municipal wastewater can provide an answer to the question if bCOD (biodegradable Chemical Oxygen Demand) and pharmaceuticals can be removed simultaneously by BioMnOx. In this case the bCOD would serve as a carbon and energy source for the heterotrophic growth of *Pseudomonas putida*. Although the development of a complex community is not necessarily negative since specialized bacteria can occur to remove the recalcitrant micropollutants, a selective pressure by using high manganese concentrations in the reactor can be applied to ensure that the bacteria population consists mainly of manganese oxidizers. High concentrations of manganese and iron are usually present in sandfilters for groundwater treatment. Addition of manganese-oxidizing bacteria could enhance the removal of residual levels of acidic pharmaceuticals present in the groundwater. Yet, the influence of iron species on the chemical oxidation with BioMnOx and the low HRT during rapid sand filtration needs to be investigated. Another application could be slow sandfiltration enriched with BioMnOx as a final polishing step for the wastewater treatment before discharge to receiving waters, since the HRT used in those systems are usually in the order of a few hours.

4 Sludge treatment and reuse

Sewage sludge is a product of centralized wastewater treatment (WWT). It consists mainly of organic matter (47%), part of which is organic matter removed from incoming wastewater and part is biomass built during the biological part of WWT (Figure 4.1).

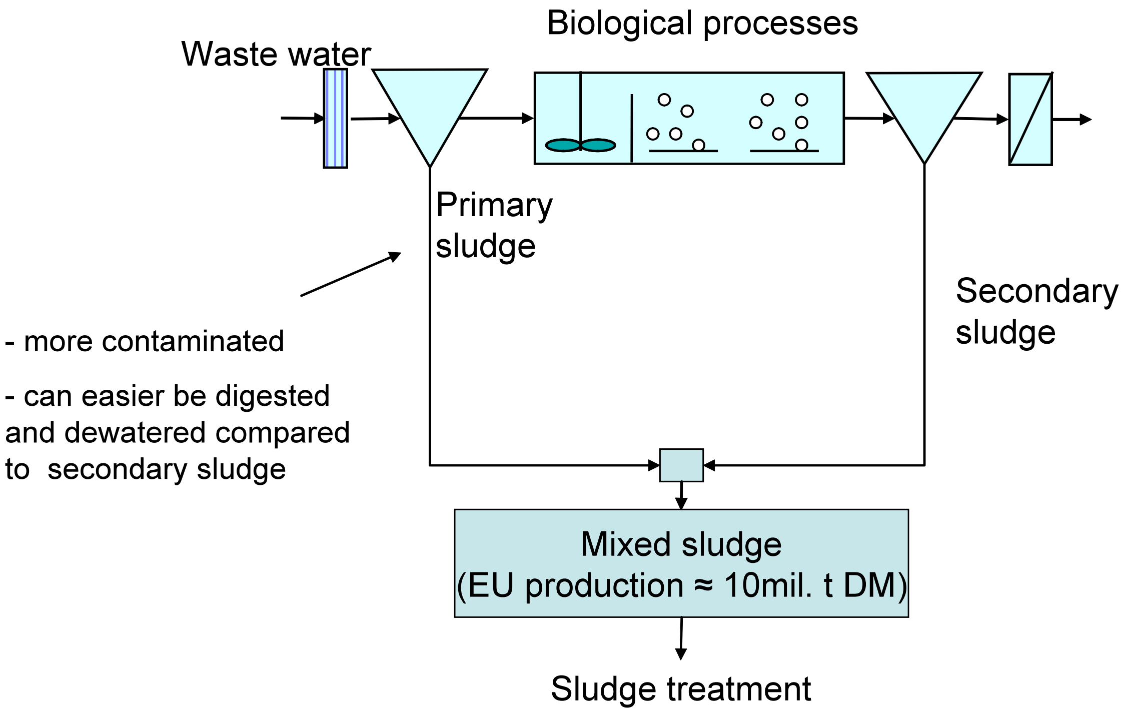

Biological processes
Waste water
Primary sludge
Secondary sludge
- more contaminated
- can easier be digested and dewatered compared to secondary sludge
Mixed sludge
(EU production ≈ 10mil. t DM)
Sludge treatment

Figure 4.1 Solids production during WWT

On average, stabilized sewage sludge contains useful nutrients and 45% organic matter, with hydrogen and carbon being the main energy source (Table 4.1a).

Table 4.1 Typical composition of digested sewage sludge a) energy content and nutrients; b) heavy metals

a)

	g/kg TS
Hydrogen	34
Carbon	220
Nitrogen	27
Oxygen	170
Sulfur	8
Chlorine	1
Phosphorus	34
Ammonium nitrogen	20
Calcium	73
Iron	75
Silicon	65

b)

	mg/kg
Cd	0.28-2.66
Cr	11.2-192.5
Cu	27.3-448.7
Hg	0.21-2.1
Ni	6.3-63
Pb	9.1-154.7
Zn	99.4-1400

**) Data are for EU member states, Source: Disposal and recycling routes for sewage sludge, Part 3, Europian Comission, October 2001*

However, the sludge contains harmful heavy metals (Table 4.1b) and the nowadays more and more observed and investigated micropollutants:

- Polynuclear aromatic hydrocarbons (PAH)
- Herbicide residues
- Polychlorinated biphenyls (PCB)
- Organo-tin compounds
- Polychlorinated terphenyls
- Phthalate esters
- Phenol
- Petroleum hydrocarbons
- Chlorinated hydrocarbon solvents and phenols
- Surfactants
- Organochlorine insecticides
- Aromatic amines
- Organophosphorus compounds

Since sludge consists of the material which had to be removed from the water due to potential risk for the people and the environment, sewage sludge itself has to be treated before it is finally disposed of in some form. Therefore, while demands on wastewater treatment are increasing, the techniques for the sewage sludge treatment have to be improved due to the more strict legislations in this area as well. The cost for sludge treatment contributes up to 50% to the overall costs of the WWTP (Khiari et al., 2004). Nowadays, at the most WWTP the mixture of primary and secondary sludge goes to stabilization and disinfection 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. The major ways for sludge use and disposal are: application to agricultural land, landfill, sea disposal and incineration. The sea dumping of sewage sludge was completely abandoned in 1980'. Land filling is also recognized as an environmental hazard in some countries (banned in Switzerland since 2000 and in Sweden since 2005). Use in agriculture is in discussion because of the increased amount of organic micro pollutants and heavy metals in the sludge. Incineration is still thought the best alternative in terms of volume and hazardous impact reduction as well as energy reuse. The amount of produced sludge, as well as the methods commonly used for sludge treatment and disposal, is given in the next table.

Table 4.2 The amounts of sewage sludge generated annually in USA and Europe (Renner, 2000)

		Disposal method (%)			
Country	**Amount*)**	**Appl. to land**	**Land filling**	**Incineration**	**Other**
Austria	320	13	56	31	0
Belgium	75	31	56	9	4
Denmark	130	37	33	28	2
France	700	50	50	0	0
Germany (West)	2500	25	63	12	0
Greece	15	3	97	0	0
Ireland	24	28	18	0	54
Italy	800	34	55	11	0
Luxembourg	15	81	18	0	1
Holland	282	44	53	3	0
Portugal	200	80	13	0	7
Spain	280	10	50	10	30
Sweden	180	45	55	0	0
Switzerland **)	215	0	0	100	0
United Kingdom, 1991	1107	55	8	7	30
United States	6900	41	17	22	20

*) million tons dry solids/yr

**) data are for 2003

Due to stricter legislations for sludge disposal and agricultural use, as well as increased pressure to recover energy and valuable nutrients from the sludge, more sustainable sludge handling methods have been introduced with constant need for improvement, including wet oxidation (Eaves et al., 2008), medium temperature gasification[1] (Burgbacher, 2006) as well as high temperature pyrolysis[2]. The major changes compared to incineration are lower or higher temperature, high pressure with oxygen and the absence of oxygen.

Any process for the final sludge treatment and disposal should results in the following:

- Reduced sludge volume
- Elimination or fixation of the pollutants
- Recovery of nutrients
- Recovery of energy (not only in the form of heat energy, while the heat energy has limited options for reuse)

Two technologies are described in this section: Sludge pyrolysis with special attention to phosphor and heavy metal recovery and the production of biopolymers and energy recovery by means of high pressure thermal hydrolysis, acidic fermentation and PHA (polyhydroxyalkanoates) accumulation for biopolymer production.

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[1] Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuel, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam.

[2] Pyrolysis is a process similar to gasification but without oxygen.

4.1 Recovery of P and heavy metals: Sludge pyrolysis

4.1.1 Process description

Ultra-high temperature sludge gasification has a potential to deliver all prerequisites mentioned above. The process is based on the pyrolysis; destruction of the organics at high temperature in the absence of oxygen. The idea of sludge pyrolysis is known for more than 20 years. However, the research done so far included processes performed at the temperatures only up to 800°C (Fonts et al., 2008; Leszczynski, 2006; Khiari et. al., 2004). The fully operational sludge pyrolysis plant in Australia (Bridle et al., 2004) runs at the temperature of 450°C. The process temperature below 800°C results in obtaining a three-phase product: gas, oily liquid as well as the solid residue (Figure 4.2). In addition, the amount of tar in the gas increases with the temperature decrease, which results in the extra costs required for the gas cleaning.

Sludge ultra-high temperature pyrolysis includes sludge exposure to the temperatures >1000°C in the absence of oxygen. Ultra-high temperature allows for avoiding the oily liquid phase in the product while *C-C* bonds will be destroyed, whereas the absence of oxygen allows for the production of CO, H_2 and CH_4 (instead of CO_2 and H_2O) so that the sludge energy content could be stored and used in other form than heat energy.

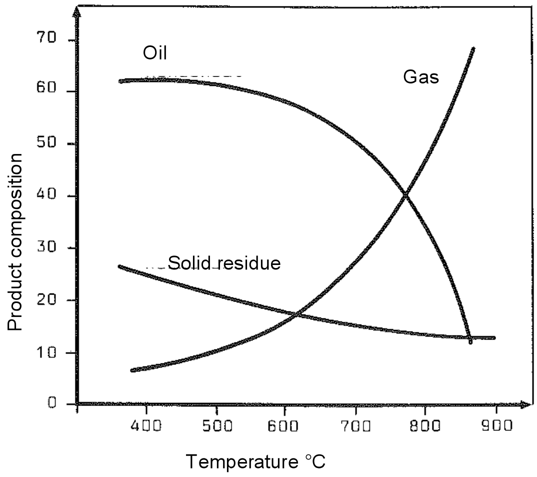

Figure 4.2 Phase distribution in the product of sludge pyrolysis depending on the process temperature

At the same time, organic micropollutants and microorganisms present in the sludge are completely destroyed. Schematic layout of the process, together with the major energy input and output, is given in Figure 4.3.

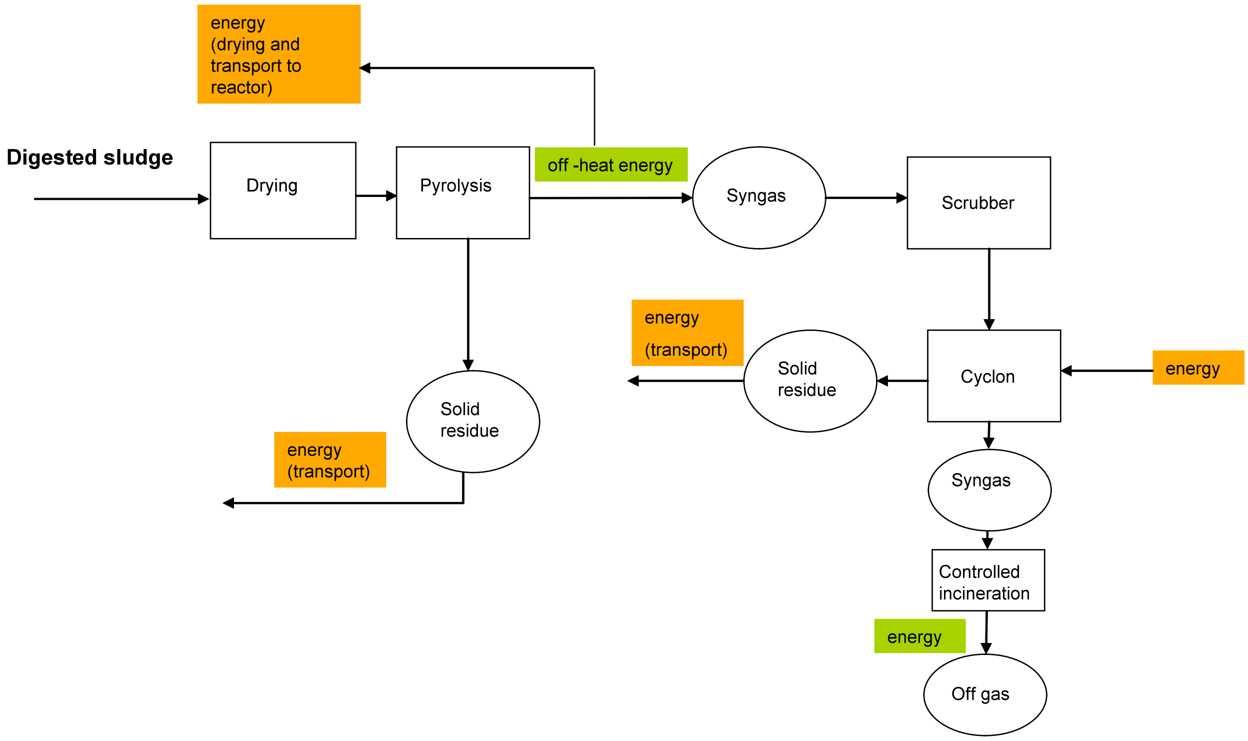
energy (drying and transport to reactor)
Digested sludge
Drying
Pyrolysis
off -heat energy
Syngas
Scrubber
energy (transport)
Solid residue
Cyclon
energy
Solid residue
energy (transport)
Syngas
Controlled incineration
energy
Off gas

Figure 4.3 Schematic layout of the ultra-high temperature gasification process

Digested and dried sludge (TS>70%) is fed to the reactor. The sludge is heated with an electrical, low-energy consumption induction system in the specially developed tube that can withstand temperatures in the range of 1000°C-1500°C over a long period of time without corrosion. As a result, hydrocarbons are converted to a gas with low content of CH_4 and high content of CO, corresponding to the composition of the syngas, which is 85 percent CO and H_2 with smaller portion of CO_2 and CH_4. Syngas can be used as an intermediate for the production of synthetic natural gas, organic chemicals, fertilizers, hydrogen, steam, transportation fuel or electric power production. The obtained solid inert inorganic product (see part 4.1.3) can be safely disposed of since it is free of any hazardous organic micropollutants. In addition, the heavy metals content of the solid residue is lower compared to the one of incineration ashes (Table 4.3) due to the increased volatilization into the process gas and the remaining heavy metals are well immobilized (for leaching properties of the solid residue see section 4.1.2).

Table 4.3 Heavy metals distribution during the incineration and pyrolysis (Kistler, 1986)

	Incineration		***Pyrolysis***			
	900°C		***700°C***		***900°C***	
	A	***B***	***A***	***B***	***A***	***B***
Cd	26.4	53.6	55.5	29.1	10.5	46.9
Cr	83.7	8.1	69.3	5.2	70.0	5.7
Cu	85.0	6.2	71.3	4.2	83.4	4.8
Hg	0.6	0.0	0.6	0.0	0.7	0.1
Ni	96.1	7.5	101.2	6.0	90.6	7.0
Pb	50.8	22.5	58.8	6.7	27.2	26.6
Zn	85.7	7.3	79.8	3.5	73.0	7.9

A - % of heavy metals input kept in the solid residue
B - % of heavy metals input transferred to the fly ash

4.1.2 Pilot plant trials and results

The pilot plant (Figure 4.4) was constructed and delivered by Pyromex, Switzerland and the trials were performed in cooperation with Eawag. The plant is located in Munich, Germany and not at the WWTP Glarnerland as originally planned, due to the possibility for Pyromex to use it as a fully commercial plant after finishing the experiments.

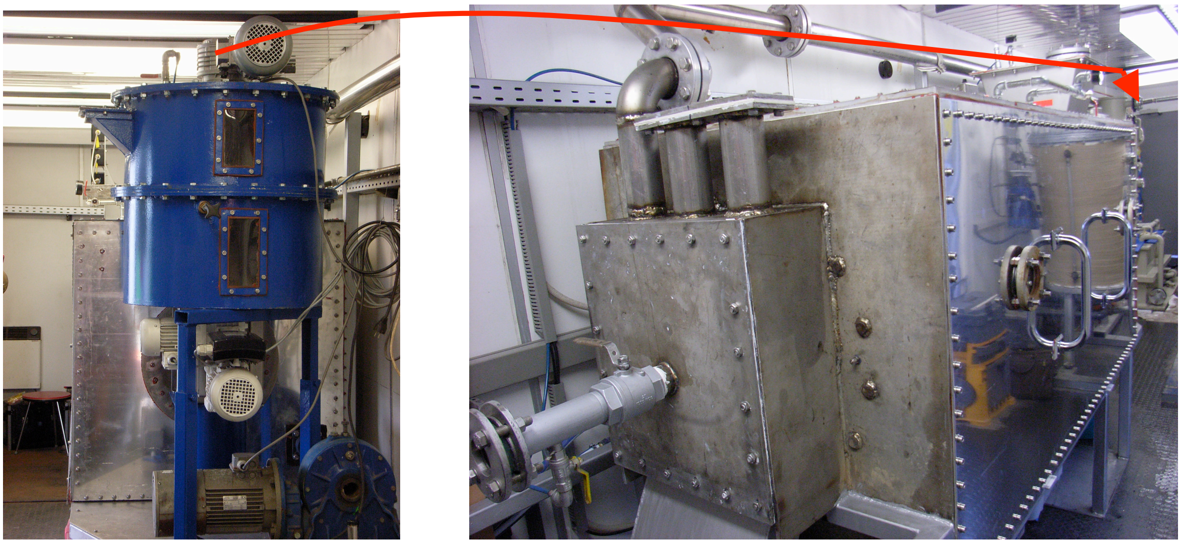

Figure 4.4 Pilot plant for ultra-high temperature gasification process with feed device (left) and reactor tube (right)

The sludge was fed to the reactor in batches of 4-6 kg. The residence time in the reactor was controlled by adjusting the speed of the rotating snail, which transported material through the reactor tube. Temperature was controlled at three points: at the beginning, in the middle and at the end of the reactor tube. The inorganic product is pushed out of the reactor, and is marked in the presented results as *solid residue*. The produced gas is transported through the pipes to the cooling and water spraying system (scrubbing). The water is recirculated and collected in a tank. A modicum of solid particles is removed with the produced gas and either stays in the cooling pipes or appears as sediment in the gas washer tank. The amount of solids collected in the cooling pipes and in the gas washer tank is approximately 10% of the total solid residue, depending on the process parameters. The gas is stored and can be further transported and reused. Due to the low heavy metals content, the solid residue could be landfilled or used either in the street construction or as a fertilizer.

The following **process conditions** were tested:

Temperature:	1200°C, 1400°C
Total solids sludge content:	70%, 80%, 90%
Residence time in the reactor:	5 min, 10 min, 15 min.

During sludge gasification at temperatures above 1000°C, only gas and solid residue were obtained as reaction products. The **obtained gas** was free of tar and consisted of CO (~40%), H_2 (~50%), CH_4 and CO_2, which is similar to the composition of syngas (lower concentration of methane and other hydrocarbons). Due to the lower content of methane compared to natural gas, the syngas has lower energy content (3-3.5 kWh/Nm^3). Gas composition from the gasification of sludge with TS content of 80% at 1200°C and 1400°C is given in Table 4 4. It does not change much with the change of the process parameters listed above. However, the energy content is slightly increased and the CO_2 fraction reduced with higher retention time.

Table 4 4 Composition of the gas obtained after gasification of sludge with 80% TS

T= 1200°C

	CO	*CO_2*	*CH_4*	*H_2*	*Σ*	*NH_3*	*SO_2*	*NO_2*	*PH_3*
time (min)	***%***	***%***	***%***	***%***		***ppm***	***ppm***	***ppm***	***ppm***
5	36.1	3.3	3.3	53.5	96.2	~10*)	x	x	x
10	38.6	2.7	2.3	55.3	98.9	~2**)	x	x	x

*) 10ppm ~ 7.5mg/m^3

**) 2ppm ~ 1.5mg/m^3

T = 1400°C

	CO	*CO_2*	*CH_4*	*H_2*	*Σ*	*NH_3*	*SO_2*	*NO_2*	*PH_3*
time (min)	***%***	***%***	***%***	***%***		***ppm***	***ppm***	***ppm***	***ppm***
5	36.4	2.8	1.3	55.5	96	x	x	x	>15*)
10	37.26	1.65	1.22	55.17	95.3	x	x	x	>15*)

*) 15ppm ~22.5mg/m^3

Noticeable is the presence of free ammonia at the lower and phosphin at higher process temperatures. Phosphorus removal and recycling is discussed in the section 4.1.3.

The solid residue, as well as the solids collected from the cooling pipes and gas washer, is analyzed for the following metals: Pb, Ni, Cr, Cd, Ca, Cu, Zn, Mn; as well as for Ptot. The obtained results for the solid residue are presented in Figure 4.5

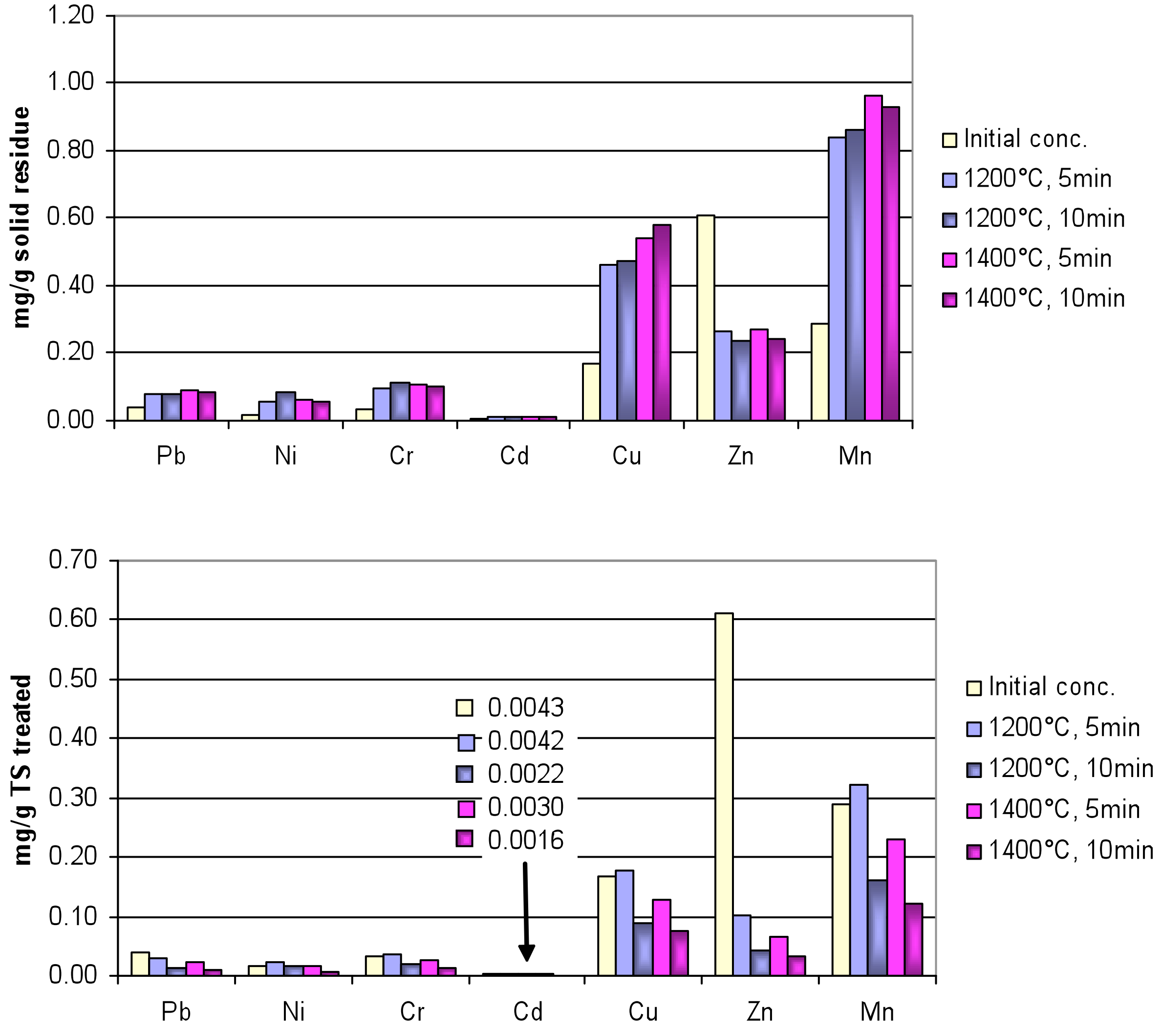

Figure 4.5 Heavy metal content of the solid residue after ultra-high temperature gasification (T = 1200 and 1400°C, detention time 5 and 10 minutes) of sewage sludge with 80% TS

The absolute concentration of heavy metals (mg/g solid residue on the graph) does not vary a lot neither with the temperature nor with the residence time variation. However, the production of solid residue (Table 4.5), gas production and heavy metal volatilization strongly depends on process temperature and reaction time. For one set of the experiments the TS mass reduction was as follows.

Table 4.5 TS reduction during the gasification process, batches of 6000 g with TS content 80%

T \ t	*5min*	*10min*
1200°C	62%	81%
1400°C	76%	87%

When all solid products are taken into calculation (solid residue leaving the reactor, solids accumulated either in the gas cooling system or in the gas washing water collection tank), the TS mass reduction of the sludge entering the gasification reactor was 60%-90%. As already mentioned a small part of the solids is lifted with the gas and accumulated either in the gas cooling system or in the gas washing water collection tank. The heavy metals in solid produced is given in Figure 4.6.

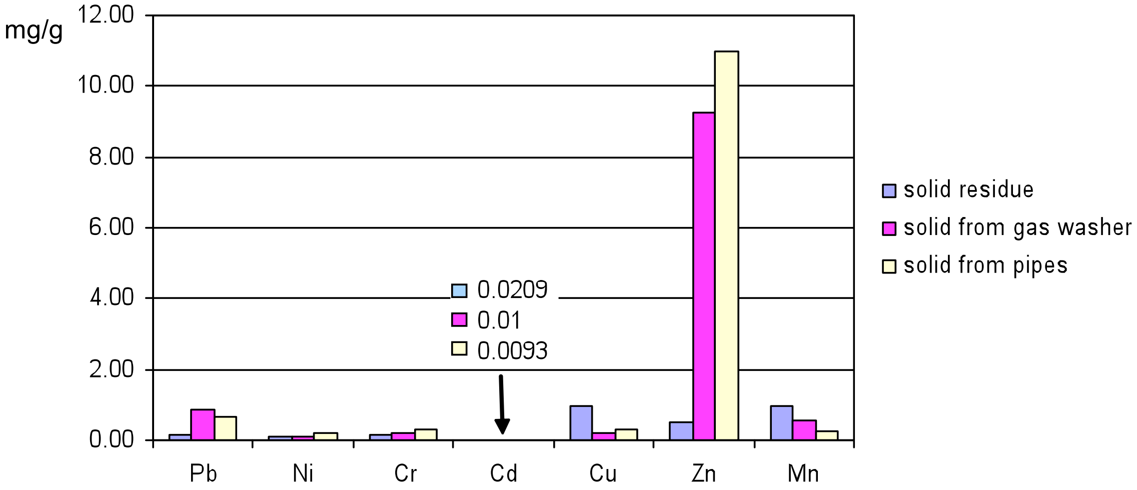

Figure 4.6 The heavy metals content of the solid output from the ultra-high temperature gasification process of the sewage sludge (90% TS, T=1200°C, t=10min)

It could be noticed that Pb, Ni, Cr and specially Zn are present in high concentration in the solids collected from the cooling pipes, with Cu, Mn and Cd staying more in the part of the inert residue that leaves the reactor. The distribution of Mn and Cu could be explained by the high melting and boiling points (1084°C and 2562°C respectively for Cu; 1246°C and 2061°C respectively for Mn). However, Cd has a tendency to stay in the inert part, which is not in correlation with low melting and boiling point (321°C and 767°C respectively). The reason could be that in the raw sludge Cd exists mainly as a carbonate while it appears as sulfide in digested sludge (used in our experiments), with the second one being more stable at the high temperatures (CdS sublimates at 970°C, while the decomposition of $CdCO_3$ starts at 280°C and ends at 500°C; Bultosa et al., 1995).

In order to evaluate the **environmental impact** of the high temperature pyrolysis solid residue, 1 g of sample was placed in 20 ml of de-ionized water and shaken for 5 days at room temperature. The results are given in Table 4.6. Neither the temperature nor the residence time had a strong influence on the solubility of the heavy metals in the solid residue.

Table 4.6 Heavy metals leaching from the solid residue of sludge with 80% TS treated with ultra-high temperature pyrolysis (1gDS/20 ml de-ionized water, 5 days at 25°C).

T	*time*	*Pb*	*Ni*	*Cr*	*Cd*	*Cu*	*Zn*	*Mn*
1200°C	*5 min*	0.63%	0.15%	0.10%	0.13%	0.04%	0.02%	0.00%
	10 min	1.42%	0.19%	0.13%	0.65%	0.08%	0.05%	0.00%
1400°C	*5 min*	0.77%	0.16%	0.09%	0.16%	0.04%	0.03%	0.01%
	10 min	0.73%	0.19%	0.10%	0.14%	0.04%	0.03%	0.01%

4.1.3 Potential for phosphorus and heavy metals recovery

Phosphorus recovery, not only removal, is recognized as a long term goal in wastewater and sludge treatment, since phosphorus is limited and non renewable. According to Herter et al. (2001) easy accessible phosphorus resources will be depleted within the next 80 years. During wastewater treatment 40-95% of the incoming phosphorus is transferred into sewage sludge, depending of the technology applied (Berg, 2005). Phosphorus content in the stabilized sludge is in the range of 18-40 g/kgTS (Siegrist et al., 1989). Digested sludge treated by the ultra-high temperature gasification process in our experiments had Ptot content of 27 g/kgTS. The phosphorus content of the major solid product of the process, as well as heavy metals concentrations, is given in the following table. The maximum values allowed for fertilizers used in Germany and Austria are stated for comparison.

Table 4.7 Heavy metals and phosphorus content of the solids residue as well as the maximum values allowed for fertilizers in some European countries (Adam et al., 2007)

TS 80%									
T = 1200°C									
	Pb	*Ni*	*Cr*	*Cd*	*Cu*	*Zn*	*Mn*	*Ptot.*	*inert residue*
time (min)	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*g*
5	0.0775	0.0583	0.0978	0.0110	0.4634	0.2625	0.8408	69.91	1840
mg/g TS	0.0297	0.0224	0.0375	0.0042	0.1776	0.1006	0.3223	26.80	
10	0.0774	0.0868	0.1110	0.0115	0.4741	0.2350	0.8628	60.58	900
mg/g TS	0.0145	0.0163	0.0208	0.0022	0.0889	0.0441	0.1618	11.36	
T = 1400°C									
	Pb	*Ni*	*Cr*	*Cd*	*Cu*	*Zn*	*Mn*	*Ptot.*	*inert residue*
time (min)	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*mg/g*	*g*
5	0.0898	0.0627	0.1067	0.0126	0.5414	0.2719	0.9614	61.44	1150
mg/g TS	0.0215	0.0150	0.0256	0.0030	0.13	0.07	0.23	14.72	
10	0.0863	0.0544	0.1026	0.0125	0.5826	0.2413	0.9273	65.62	630
mg/g TS	0.0113	0.0071	0.0135	0.0016	0.0765	0.0317	0.1217	8.61	
innit. conc in sludge	0.0405	0.0177	0.0313	0.0043	0.1691	0.6101	0.2888	27.42	
Limit values for fert. D	0.1500	0.0800	-	0.004*)	0.0700	1.0000			
Limit values for fert. A	0.1000	0.1000	0.6670	0.011**)	0.7780	3.3330			

**)no limit value, only obligation to the label*
***)related to the P content of 6.5%*

The content of Cu in the solid residue exceeded the maximum value for fertilizer in Germany but not for the Austria. With 6.5% phosphorus, the solid product could therefore be applied as a fertilizer since the level of phosphorus in the conventional fertilizer such as single super phosphate (SSP) is 8% Ptot (18% P_2O_5), (Adam et al., 2007). Figure 4.7 gives a better overview of the phosphorus content of the solid residue depending on the process parameters.

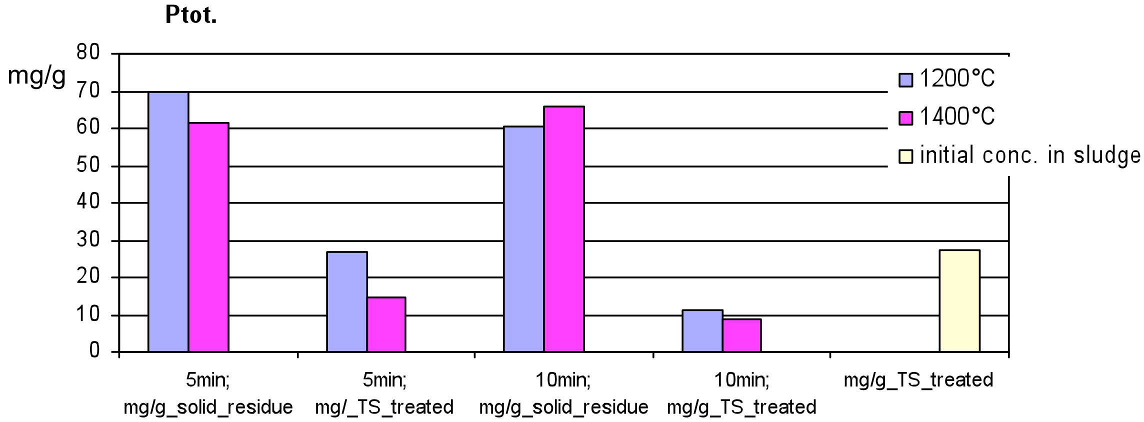

Figure 4.7 Phosphorus content of the solid residue

As it can be seen from the results presented, a longer residence time increases the transfer of phosphorus from the solid residue to the gas phase. Since a shorter residence time gives a higher amount of residue which is not transferred to the gas phase, the phosphorus will mainly stay in the solid residue for temperatures < 1200°C and a residence time of 5 minutes. The phosphorus content of 6%-9% in the pyrolysis residue is comparable with the phosphorus content of the ashes obtained after sewage sludge incineration, which was in the range of 4.8%-10.9% (or 11%-25% when calculated as P_2O_5), (Adam et al., 2007).

The bioavailability of the recycled phosphorus is tested by dissolving the residue in 2% citric acid (Table 4.8). A shorter residence time gives a slightly better phosphorus bioavailability and a higher P fraction remaining in the reactor residue.

Table 4.8 Phosphorus bioavailability

	5min		***10min***		
	init.conc.in res. (mg/	***% leached***	***init.conc.in res. (mg/g)***	***% leached***	***init.conc.in sl. (mg/g)***
T					
1200°C	69.91	12.60%	60.58	9.92%	27.42
1400°C	61.44	11.90%	65.62	11.84%	

4.2 Recovery of organics: Production of biopolymers from biosolids

4.2.1 Background

Biosolids is the term used to describe the solid by-products from sewage treatment processes. Biosolids are a burden for the operation of wastewater treatment plants since handling and disposing of biosolids are a major cost and can cause long-term greenhouse gas emissions if landfilled. In the context of this technology, however, biosolids represent a high volume, renewable resource rich in carbon, nitrogen and phosphorus that can be transformed into usable products, i.e., bioplastics and energy (Figure 4.8). Bioplastics, such as polyhydroxyalkanoates (PHAs), are polymers synthesised by bacteria and can be degraded biologically and be reintegrated into the Earth's short-term carbon cycle, in contrast to conventional oil-based plastics currently being extensively used. Therefore, the objectives of the proposed process and technology developed during this research project are: (i) to maximise the production of volatile fatty acids (VFAs) to be used as feedstock for biopolymer synthesis from pretreated waste activated sludge (WAS), and (ii) to produce optimally PHAs based on this VFA-rich stream.

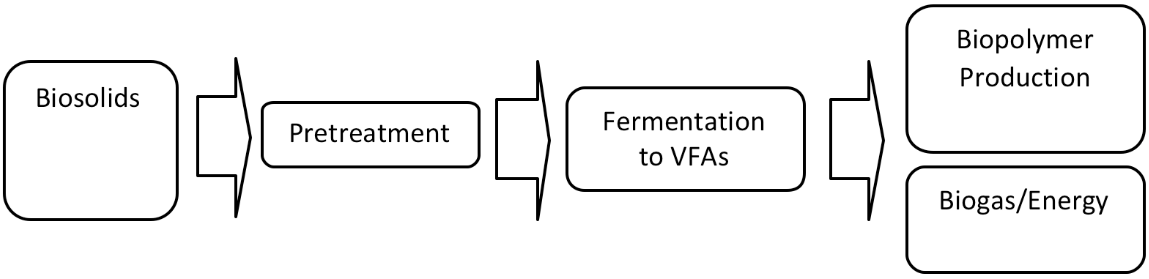

Figure 4.8 Strategy for utilising biosolids to produce biopolymers and energy. Volatile fatty acids (VFAs) produced during fermentation are the ideal feedstock for biopolymer production.

4.2.2 Potential areas of application

PHA bioplastics can replace parts of the market of conventional plastics such as polypropylene and polyethylene since PHAs possess similar thermoplastic properties (Lee, 1996). Furthermore, PHAs can be produced by open, mixed bacterial cultures utilising inexpensive and renewable carbon sources, namely waste streams, e.g., fermented pretreated biosolids.

The technology investigated in this research is directly applicable to the wastewater treatment industry as the feedstock, biosolids, is generally an unwanted by-product. For example, a moderate sized wastewater treatment facility (500 000 PE) handles in the order of 50 000 wet tonnes of biosolids per year. Biosolids are a potential substrate since they are abundant, regular in concentration and contain biodegradable carbon; however, they need to be solubilised and may contain a large fraction of inert matter. The fundamental outcomes of the research as translated into the proposed process and technologies have broader application to acidogenic fermentation and mixed culture production of PHA using high-strength waste streams.

4.2.3 Stage of development

Although the fundamentals of the proposed technology are based on several years of research and development, the technological application and evaluation to the specific case of biosolids requires further optimisation. Among these considerations are optimal bioreactor operation, downstream processing, and energy use. The process proposed at this point is based on lab-scale tests only and pilot-scale testing will be required for further implementation.

4.2.4 Technology description

4.2.4.1 Biosolids pretreatment

Hydrolysis of particulate material to soluble substances is considered as the rate-limiting step in anaerobic digestion of biosolids. Therefore, pre-treatment technologies have been used to enhance the digestibility of waste activated sludge (WAS) and increase biogas production (Ødegaard, 2004). High pressure thermal hydrolysis (HPTH) (e.g., Cambi process) is one of the pre-treatment processes available that solubilises suspended matter by hydrolysis at high temperatures (100-180°C) and pressure (6 bar) at a retention time of approximately 30 min. HPTH generates a waste stream that is amenable to high rate acidogenic fermentation and the production of volatile fatty acids (VFAs) that can be further utilised in the biological production of PHAs by mixed cultures, as demonstrated in this research. Although HPTH reduces overall sludge production in the plant, disinfects the sludge, improves sludge viscosity and increases sludge dewaterability, it leads to increased levels of odorous compounds (e.g., H_2S) (Neyens and Baeyens, 2003), and to a brown liquid high in ammonium and soluble inerts. Our analyses indicate that HPTH pretreatment decreases the total suspended solids (TSS) by up to 30%, solubilising the total organic carbon from 5 to 50%.

4.2.4.2 Acidogenic fermentation

Fermentation refers to the conversion by acidogens of substrate to alcohols and organic acids. With regard to the generation of feedstock for biopolymer production, the objective is to ferment organic material into VFAs. In continuous fermenters, the retention time should be long enough to support the growth and activity of acidogens, but short enough to washout slow growing VFA-consuming methanogens. The growth of methanogens can also be inhibited by the generally acidic pH of the fermenter (5.5-6.5). For fermenters treating complex waste streams, retention times of between 1 and 4 days are typically employed. Fermentation of primary sludge has been widely reported, but the feasibility of WAS fermentation has been limited by its relatively low biodegradability. This research shows that fermentation of thermally hydrolysed waste activated sludge (HPHT-WAS) leads to high VFA yields (0.50 $gCOD_{VFA}$ per g of soluble chemical oxygen demand (SCOD).

4.2.4.3 Selection of PHA-storing organisms

Enrichment of PHA-accumulating organisms is conducted by exerting a selective pressure via aerobic dynamic feeding (ADF) exposing the biomass to periods of substrate availability (feast) followed by substrate limitation or starvation (famine). During feast, VFAs are stored as PHAs and during famine the stored PHAs are consumed as a carbon and energy source by the accumulating bacteria, giving them an advantage over non-accumulating bacteria. ADF can be conducted continuously in an activated sludge system with a selector (Bengtsson et al., 2008) or in batch in sequencing batch reactors (SBRs). Exposure to feast conditions has to be ≤ 20% of the total aerobic exposure or cycle length in SBRs (Figure 4.9). Other important design considerations are the retention times, both hydraulic and sludge retention times (HRT and SRT), the length of the cycle and organic loading rates (OLRs).

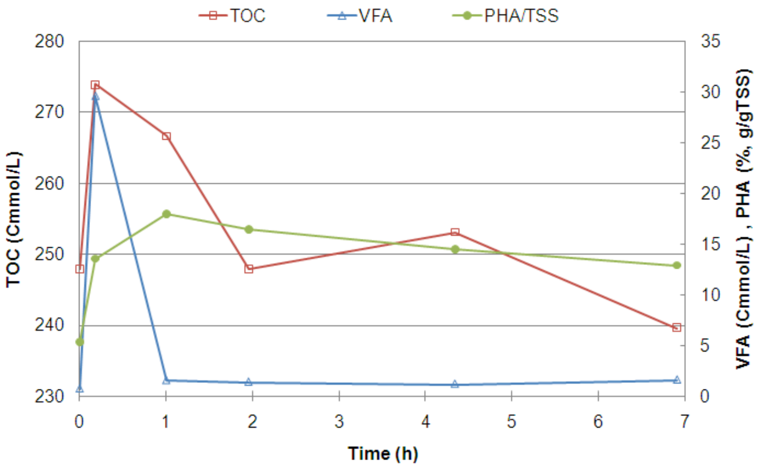

Figure 4.9 Experimental profiles of total organic carbon (TOC), VFAs and biomass PHA content during a cycle in an SBR selecting for PHA-storing organisms. PHA production reaches a maximum immediately after VFA consumption during the feast phase, which corresponds to less than 14% of the cycle basedon VFA availability.

4.2.4.4 PHA accumulation by the enriched biomass

Bacteria are harvested from the enrichment reactor and exposed to periodic substrate spiking in order to increase the PHA content of the biomass. Fermented biosolids can be used as substrate for PHA accumulation, but since the composition of the accumulated PHA can be manipulated based on the VFA composition of the substrate, an acetate/butyrate-rich stream can be used if polyhydroxybutyrate (PHB) is preferred as main monomer without polyhydroxyvalerate (PHV). Our experimental results indicate that if the enrichment is successfully conducted, a complex waste stream, rich in a broad range of VFAs, can be used for accumulation despite containing non-VFA biodegradable compounds, and high levels of nutrients. Therefore, the same fermented feed used for enrichment can be used for PHA accumulation.

4.2.4.5 Downstream processing (polymer extraction and purification)

Conventional solvent-based extraction and purification of the polymer was conducted in this research at lab-scale for characterising the polymer; however, the technology for larger scale production would require optimisation and further development. A series of downstream processing units similar to those employed at large-scale pure culture PHA production facilities can be at this point envisioned: homogenisation, centrifugation, solvent rinsing, centrifugation with buffer washing, and drying (Gurieff and Lant, 2007).

4.2.5 Process description

4.2.5.1 Integrated process

This technology considers the utilisation of biosolids as carbon-rich resource for biopolymer production in tandem with biogas/energy generation. A proposed overall flow diagram of the process is presented in Figure 4.10 based on the findings of this research. Performance parameters are described below with exception of the downstream processing units (Figure 4.10).

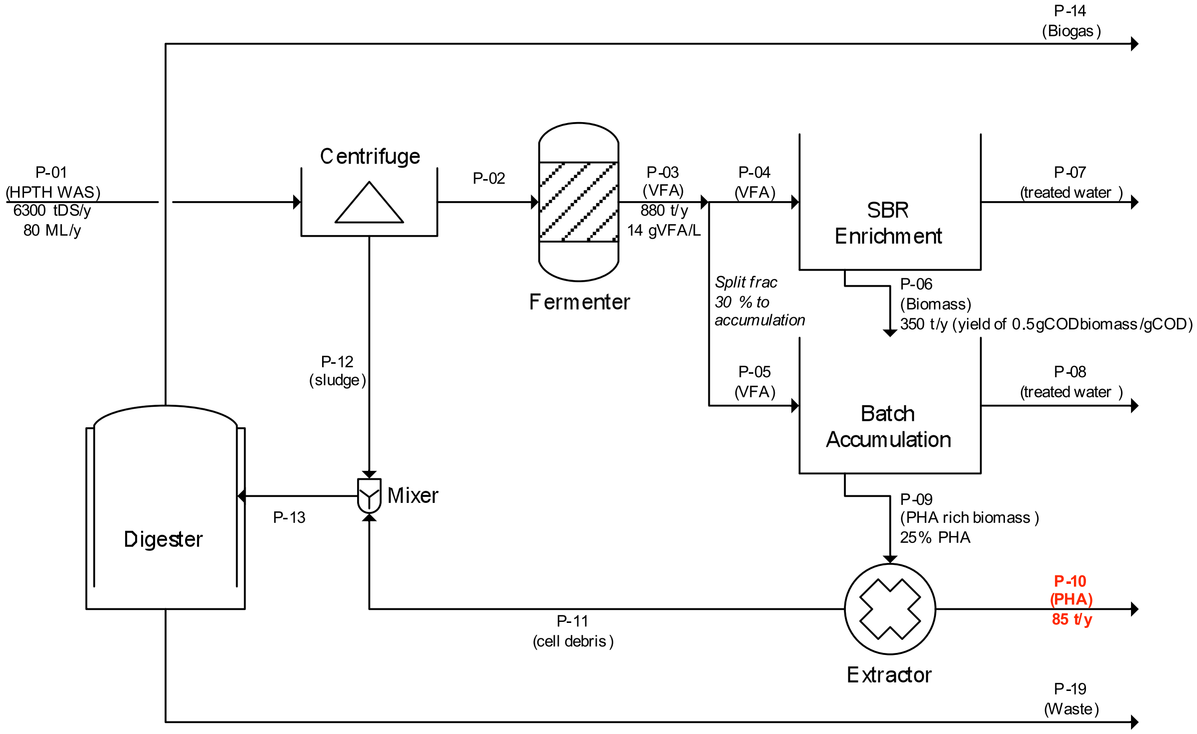
P-14
(Biogas)
P-01
(HPTH WAS)
6300 tDS/y
80 ML/y
Centrifuge
P-02
Fermenter
P-03
(VFA)
880 t/y
14 gVFA/L
P-04
(VFA)
SBR
Enrichment
P-07
(treated water)
Split frac
30 % to
accumulation
P-06
(Biomass)
350 t/y (yield of 0.5gCODbiomass/gCOD)
P-12
(sludge)
P-05
(VFA)
Batch
Accumulation
P-08
(treated water)
Digester
P-13
Mixer
P-09
(PHA rich biomass)
25% PHA
P-10
(PHA)
85 t/y
P-11
(cell debris)
Extractor
P-19
(Waste)

Figure 4.10 Proposed process flow sheet for producing PHA biopolymers from thermally hydrolysed sludge (Including flow rates of major streams). ***Basis: HPTH-WAS flow (6300 tDS/y) from Oxley Ck (Brisbane, Australia) CAMBI process***

Permeate collection. A centrifuge (achieving a 90:10 permeate to sludge separation) has been used to remove unwanted material. The soluble components (P-02) are used as the major substrates for the fermenter, and removing the suspended fraction decreases fermenting volume requirements. The waste solids (P-12) can be digested for biogas production.

Acidogenic fermentation. Our research shows that the fermenter can be operated with a residence time of 1-2 days (Table 4.9) under which conditions the VFA production rates are high due to high throughput in comparison to fermenters treating unpretreated WAS, which would require a larger fermenter.

Table 4.9 Experimental operating conditions and performance of fermenter fed with thermally hydrolysed biosolids

Operating parameters	**Value**
HRT (d)	1
Loading rate (gSCOD $L^{-1}d^{-1}$)	30
Temperature (^{o}C)	42
VFA yield (gCOD $gSCOD^{-1}$)	0.50
VFA production rate (gCOD $L^{-1}d^{-1}$)	15

For the case study presented, the fermenter would have to be sized to process 200 m^3 day^{-1}. Consequently, to support a 1 d retention time, a fermenter in the order of 200 m^3 would be required. The VFA yield for 1 d retention time is in the order of 0.5 $gCOD_{VFA}$ $gSCOD^{-1}$ (or 15 $gCOD_{VFA}$ L^{-1}). The relative proportions of VFAs produced (on a COD basis) are shown below in Figure 4.11:

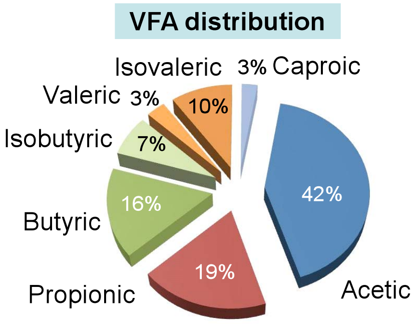

Figure 4.11 Spectrum of VFAs produced (avg 1.5gCOD/gVFA)

Enrichment of PHA-storing organisms. The operating conditions of the SBRs investigated in this research enriching for PHA-accumulating organisms are presented in Table 4.10. Research results indicate that 70% of the soluble COD will be removed with a 100% removal of COD_{VFA}, and that soluble ammonium and orthophosphates will be removed with 75% and 60% efficiencies. Therefore, the treated liquid stream (P-07) will require further treatment with respect to nutrients an inert COD and will be directed to the wastewater treatment plant or to a separate treatment, as generally done with the liquid waste streams from WAS anaerobic digesters.

Table 4.10 Operating parameters used in experimental SBRs enriching for PHA-accumulating organisms from fermented HPHT sludge

Operating parameters	Range of values proposed
HRT=SRT (d)	6
Maximum COD_{VFA} concentration per cycle (g L^{-1})	1
Cycle length (h)	8
OLR (g COD_{VFA} $L^{-1}d^{-1}$)	3

PHA accumulation. Our research results indicate that a batch reactor for PHA accumulation operated with a retention time of 8 h yields 0.20 gPHA $gCOD_{VFA}^{-1}$ with a PHA biomass content of 25% (gPHA $gVSS^{-1}$) and production rates of 2 up to 5 kgPHA $m^{-3}_{reactor}$ d^{-1}, depending on the biomass levels in the reactor. Further treatment may be required from stream P-08. When fermented HPTH biosolids were used as feed for the accumulation, a polymer with a 75%mol hydroxybutyrate and 25%mol hydroxyvalerate content was obtained.

The polymer obtained was elastic with high thermal stability, making it desirable for different polymer applications.

PHA extraction. Downstream processing is necessary in order to extract the PHA from the biomass in stream P-09. A number of options are available and include a series of pretreatment units, solvent extraction and drying as employed in pure-culture PHA production facilities (Gurieff and Lant, 2007).

4.2.5.2 Process applicability

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 WAS turnover (Figure 4.10, e.g., 6 300 tDS y^{-1}). Although one strength of the investigated process lies on the pretreatment that allows a higher throughput of biosolids leading to higher VFA production rates than unpretreated WAS, further optimisation of the bioreactors is required with respect to operating conditions and organic loading handling. In addition, the downstream processing units for polymer extraction need to be tested and their operating conditions optimised, but this was outside the goals of this research work. The utilisation of the fermented stream as a source of VFAs for PHA production was demonstrated with this work and deserves consideration in full-scale applications, especially since the produced biopolymer represents a value-added product from waste carbon and complements energy production as treatment byproducts.

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