

NEPTUNE

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

Contract-No. 036845

A Specific Targeted Research Project
under the Thematic Priority 'Global Change and Ecosystems'

Work Package 5 · Dissemination

Deliverable 5.4 · Catalogue with criteria for evaluating technologies

Due date:	Month 40
Actual submission date:	31/08/2010
Start date of project:	01/11/2006 Duration: 41 months
Deliverable Lead contractor: (Organisation name)	Aquafin
Participant(s) (Partner short names)	Aquafin, AnoxKaldness AB, AWMC, BfG, Cambi, IRSA, DPU, Eawag, Hunziker, UniFra, LabMET, ModelEAU, Pyromex, SiluetB
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Dissemination Level:	
(Public,	
<u>PP</u> Restricted to other <u>P</u> rogramme <u>P</u> articipants,	PU
<u>RE</u> stricted to a group specified by the consortium,	
<u>C</u> onfidential only for members of the consortium)	

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Content

Preface	1
Author list.....	2
Content.....	4
I. Nutrient removal.....	6
II. Micropollutants and ecotoxicity removal	9
III. Sewage sludge management	15
References.....	24
IV. merging technologies	25
V. Fact sheets	27
1 Sludge triage	28
2 Ultrahigh temperature pyrolysis	36
3 Separate hospital wastewater treatment	43
4 Wet oxidation	51
5 Thermal hydrolysis	58
6 Production of biopolymers from waste biosolids	68
7 Instrumentation, control and automation	73
8 Zeolite addition for improvement of WWTP performance.....	84
9 Combined nitrification/Anammox in a sequencing batch reactor	93
10 Full scale wastewater ozonation	100
11 Powdered activated carbon	110
12 BioMAC.....	119
13 Ferrate technology	127

14	Biometals	137
15	Nitrifier enriched culture (NEC)	145
16	Microbial fuel cells	151

I. NUTRIENT REMOVAL

Nutrient discharge and eutrophication of surface waters is of concern in many urbanised areas. In the last decades, thanks to European legislation, progressively more wastewater treatment plants have been built for the removal of ammonia, nitrate, and phosphate that has led to significantly better surface and ground water quality.

In the 1970's and 1980's, wastewater treatment plants (WWTPs) were built for carbon removal, if there was wastewater treatment at all. Oxygen was depleted in many water bodies, because of the BOD in discharges, but in others mainly due to eutrophication and subsequent algae bloom. Hence, around 1990 many surface waters were virtually dead and public awareness arose at the same time. On 21 May, 1991 the directive 91/271/EEC of the European Economic Community on urban wastewater treatment was adopted. This directive obligated European countries to collect, and treat all discharges of wastewater of agglomerations with more than 2000 people equivalent by the end of 2005. Although this directive was mainly concerned with removal of organic load and suspended solids in normal regions, including nutrients removal in sensitive areas, water quality has ameliorated a lot since then. For example, while there was a slight increase in inhabitants in Flanders municipal nitrogen and phosphorus discharge towards surface waters has decreased with roughly 40% between 1990 and 2006, whereas the industrial discharge has decreased by more than 60% in the same period¹.

Simultaneously and unrelated to water treatment, there was broad public concern related to phosphate content of detergents in the 1970's and 1980's. In the late 1980's and beginning of the 1990's, there was a move to reduce the phosphorus concentration in detergents, such as the amount of sodium tripolyphosphate, and a switch to phosphorus alternatives, such as zeolites, for usage in detergents.² Voluntary actions of the industry were supported by legal bans on phosphorus in laundry detergents in some member states of the EU. This move resulted in reductions of phosphorus load up to 40%. Because of increasing wastewater collection and treatment, significant reductions of municipal nutrients discharge were obtained (for example - 38% of total nitrogen in Flanders by 2005). By the end of 2000 69% of the agglomerations in the EU with more than 15000 PE had secondary treatment of municipal wastewater, although notorious differences in treatment frequency existed (for example 100% treated for Germany and Austria, 89% for the UK and around 50% for Greece, Ireland, and Portugal).

On 23 October 2000, the European Council adopted the European Water Framework Directive 2000/60/EC³ which focuses on water quality. The directive imposed member states to have good ecological water quality in all waters by 2015 by organizing water management on a river basin scale. Classically wastewater treatment plants are designed based on rules of thumb, frequently resulting in overdimensioned or not optimal working installations. Hence, a different approach to treatment plant design and operation was necessary. This not only implies further investments into amongst others sewage systems, but also more profound removal of nutrients in wastewater treatment plants. Cost and benefit assessment were seconded by European projects such as the CD4WC project. A logic and necessary approach is further upgrading of WWTPs towards nitrogen and phosphorus removal.

Moreover, because correct alteration of aerated and non aerated periods in activated sludge systems is of significant importance for nutrient removal, there is a strive towards online control of aeration systems. This move from manual aeration control to aeration controlled by online

¹http://www.milieurapport.be/Upload/Main/MiraData/MIRA-T/02_THEMAS/02_13/KWALITEITOPPERVLAKTEWATER_MIRA-T2007.PDF

² http://ec.europa.eu/environment/water/pollution/phosphates/pdf/phosphates_xsum.pdf

³ <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:EN:NOT>

measurements of relevant parameters such as dissolved oxygen, ammonia, and nitrate is also supported by decreasing prices in online sensors from more than 25 thousand euro a decade ago to roughly ten thousand euro at the moment and even less for newer online analytical techniques. Profound online control systems on municipal wastewater treatment plants provide the opportunity to further reduce emissions very cost-effectively. They may not only save significant amounts of energy and dosage of chemicals, but may also increase nutrients removal by up to 5-10% if the best, plant-specific, aeration strategy with optimal settings is used. Driven by European and national legislation consents on nutrients are increasingly tightened the last two decades. In order to obtain good water quality, intensive dosing of chemicals and/or tertiary treatment of the wastewater may be required.

Because investments to reduce environmental impact of discharges is increasingly expensive with lower concentration of phosphorus and nitrogen, a fourth approach is computer based modelling of sewer systems and WWTPs or integrated modelling of water basins for targeted upgrading of investments (see e.g. [1]).

Several fields of research provide significant margins for enhancing nutrients removal. Since biological phosphorus removal was discovered, its application became popular, although the process and its relation to nitrogen removal is still not completely understood. In addition, since nitrite production is an intermediate step in nitrogen removal, being able to control its production through online measurements may enhance nitrogen removal and reduce environmental impact (also because of suspected relation towards laughing gas production in WWTPs, a strong greenhouse gas). Additionally, separate treatment of ammonia rich sludge liquid with the nitrification/anammox process improve overall nutrient removal and in parallel reduces energy consumption and greenhouse gas emissions [2].

Although water quality is ameliorated a lot since the European directive on urban wastewater, the situation in Europe is far from perfect and region (and geology) dependent. For example, in Belgium some 35% of surface waters in the northern part, Flanders, whereas 70% in the Southern part, Wallonia, are of good ecological quality.

To obtain a good quality everywhere, there is a need of further investments in European member states. We have now in a situation where further emission reductions of nutrients are increasingly costly and require more expensive treatment techniques. For example, it may be possible to reduce emissions in a more pronounced way, but at the expense of for example energy intensive techniques, such as reverse osmosis, or intensive dosing of chemicals whose production also releases emissions with environmental impact. Therefore, more initiatives for optimal environmental impact reduction of nutrients need to be performed and at the same time further research towards efficient and cost-effective investments are necessary.

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II. MICROPOLLUTANTS AND ECOTOXICITY REMOVAL

Contamination of surface waters in urbanised areas is mainly a result of the high input of municipal or industrial wastewater [1]. In many regions contamination with macropollutants (acids, salts, nutrients and natural organic matter occurring at $\mu\text{g/L}$ to mg/L concentrations) is increasingly under control. A progressive wastewater treatment allowed for the reduction of eutrophication as shown e.g. for Lake Constance (Germany) leading to an amelioration of water quality and recovery of the ecosystem [2]; [3].

However, micropollutants – trace organic contaminants occurring at ng/L concentrations or even below – attract more and more attention regarding their impact on aquatic ecosystem health. Thousands of different chemicals are introduced in the aquatic environment on trace levels [1] but only a few were characterized for ecotoxicity at environmentally relevant concentrations yet. In recent years, especially pharmaceuticals and personal care products (PPCPs) gained increasing interest as so called emerging contaminants which are regularly and highly consumed by private households, hospitals, retirement homes and radiological practises. While several pharmaceuticals are metabolized in the body and a mixture of the unaltered drug and its metabolites are excreted by urine and faeces, ingredients of personal care products reach the wastewater mainly due to their use in rinse-off products ([4]; [5]. Pharmaceuticals and personal care products (PPCPs) often exhibit a high persistency or pseudo-persistency and high polarity [6]. Thus, these compounds are often removed incompletely by biotransformation or sorption on activated sludge in conventional biological treatment plants and continuously released into the aquatic environment [7]; [8]. Pharmaceuticals have a designated biological activity but therefore also the potential to endanger non-target species by negatively affecting their metabolism even at much lower concentrations: The pharmaceuticals carbamazepine, diclofenac and metoprolol have been shown to impair the general health condition of rainbow trouts via cytological alterations of liver, kidney and gills with a lowest observed effect concentration (LOEC) of $1 \mu\text{g/L}$ [9]. 17α -ethinylestradiol (EE2) is considered to be the most potent estrogenic compound for fish inducing vitellogenesis at a LOEC of 0.1 ng/L in rainbow trouts [10] and leading to reduced egg fertilisation success and skewed sex ratios toward females of fat head minnows at a LOEC of 0.32 ng/L [11]. The xenoestrogen bisphenol A is known to induce a superfeminization syndrome in the prosobranch snail *Marisa cornuarietis* at concentrations as low as $1 \mu\text{g/L}$ and an increased reproductive output could be observed at low ng/L concentrations [12]. The anti-depressant fluoxetine reduced the embryo number of the prosobranch snail *Potamopyrgus antipodarum* with a no observed effect concentration (NOEC) of $0.47 \mu\text{g/L}$ [13], while EE2 increased the embryo number at a NOEC of 5 ng/L [14]. According to Schwarzenbach et al. [1] and Wick et al. [15] conventional wastewater treatment processes eliminate such substances often not sufficiently. Consequently micropollutants rather commonly occur at levels exceeding effect concentrations in waste- and surface waters [16]; [17]. Carbamazepine, diclofenac and metoprolol for example are reported at low $\mu\text{g/L}$ concentrations in wastewater treatment plant effluents [18]; [19]. EE2 occurred at median concentrations of $1\text{-}9 \text{ ng/L}$ in German and Canadian wastewaters [20] and bisphenol A could be detected in German surface waters at concentration from $<20\text{-}1942 \text{ ng/L}$ [21]. Therefore, negative and even population relevant effects for aquatic wildlife are to be expected, especially with regard to mixture toxicity and the possibility of

additive effects [22]. An example is that the estrogenic activity of wastewater was linked to reduced fertility of fish [23]. It has also been shown that vitellogenin induction in carp, which was used as biomarker for estrogenicity, occurred when fish were exposed to ambient water containing 25% treated wastewater [13]. Moreover Liney et al. [24] demonstrated lowest observed effect concentrations for genotoxicity, estrogenicity and nephrotoxicity at 20%, 40%, and 80% wastewater treatment plant effluent concentrations, respectively. Since PPCPs and their transformation products have been detected in groundwater [16]; [25] it is considered that micropollutants in waste- and surface waters also have the ability to negatively impact drinking water [16].

Besides, in the European Union the reduction of the contamination of surface waters with hazardous substances is defined by the Water Framework Directive requiring a 'good status' for all coastal and inland waters until 2015 [26]. One tool is the implementation of environmental quality standards (EQSs) for mono substance pollutants exhibiting a significant risk to the aquatic ecosystem. The discharge of such compounds, classified as priority substances, is envisaged to be progressively reduced by 2025 or 5 years after inclusion in the list for priority substances, respectively.

However, till now so called 'emerging contaminants' are only marginally addressed and pharmaceuticals and personal care products (PPCPs) are not included in this list. But the latter has to be reviewed at least every four years and provisions have been made to add several hazardous emerging contaminants. Amongst others the inclusion of diclofenac, EE2 and carbamazepine is discussed and additionally recommended by the European Parliament since 2007 [27]. Moreover EQSs meanwhile have been proposed for several PPCPs based on reliable ecotoxicity data (e.g. diclofenac: 0.1 µg/L, EE2: 0.03 ng/L, carbamazepine: 0.5 µg/L; [28]; [29]). Unfortunately, some PPCPs exceed the EQSs in surface waters of some urbanised regions. That is, *inter alia*, a result of the fact that conventional wastewater treatment plants are not designed for appropriate removal of PPCPs [6].

This is why the implementation of strategies for micropollutant removal from wastewater should become an essential element of wastewater treatment management.

Thus at short term perspective end of pipe techniques could play an important role to reduce the contamination of highly polluted surface waters. At present the most prominent advanced techniques are ozonation and activated carbon treatment subsequent to conventional wastewater treatment with activated sludge. Both techniques are most promising regarding the reduction of a broad range of micropollutants [30]; [31]; [32]. Nevertheless, chemical analyses normally focus on parent compounds while transformation products are largely unknown and thus often not considered [25]. Therefore ecotoxicity tests are indispensable for a qualitative evaluation of advanced treatment methods. Meanwhile toxicity reduction of wastewater through ozonation has been observed in several studies based on *in vitro* bioassays [33]; [34]; [35]. Most notably is the decreased endocrine activity [36]; [34]; [35]; [37] what could be a population relevant benefit of advanced wastewater treatment for sensitive species in highly contaminated surface waters.

However, ozonation carries the inherent danger to produce toxic oxidation byproducts because chemical compounds are often not mineralized entirely but transformed to unknown intermediates [38]; [39]; [40]; [41]; [42]. For example, Benner and Ternes (2009) showed that the ozonation by-products of the beta blocker propranolol mainly contained aldehyde functions which might be of (eco-)toxicological relevance. Therefore it should be investigated to what extent the chemical contamination as well as toxicity decreases with advanced wastewater treatment steps. But additionally a potential toxicity increase after ozonation and the efficiency of subsequent post-treatments - as sand filtration - to remove toxic transformation products

have to be evaluated.

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III. SEWAGE SLUDGE MANAGEMENT

INTRODUCTION

Wastewater (WW) treatment and the management of the sludge produced are global issues, with growing challenges, that must address the concerns of all of the stakeholders, including the facility administrators and operators, the regulators, the politicians, the scientific community, the wastewater generators, the taxpayers and the general public [1].

The volume of the sludge extracted from primary and secondary settling tanks is about 2% of the volume of treated domestic WW. In spite of its negligible volume, sludge management entails very high capital and operating costs, which can be accounted as high as 50% of the total costs of the WW treatment plant, i.e. 25-35 €/ (person × year) including disposal costs to be evaluated in 2-20 €/ (person × year).

Typical treatments for a large WW treatment plant include a first phase of concentration, generally carried out by gravity thickening, a biological aerobic or anaerobic stabilization, aimed to reduce biodegradable solids, odours and pathogens, and mechanical dewatering by centrifugation, belt-pressing or filter-pressing. In most cases sludge processing is designed according to the conventional systems, which might not be suitable for producing sludge with proper characteristics for its final disposal or utilization according to the legislative standards and avoiding any detrimental effects for the environment and any risk for the human health.

The current situation in most European countries is quite diverse. Table 1 shows the current sludge disposal options in some European countries [1].

Table 1 Current disposal options in European countries (% of sludge produced)

	Landfill sites	Thermal treatments (incineration)	Composting	Agricultural utilisation	Non agricultural utilisation	Other
European Union	18	23	7	45		7
Austria		35	50	15		
Bulgaria	100			Only few cases		
Czech Republic	13	<1	50	17		20
Finland			73	3		
Flanders		88			12	
Germany	3-6	20 (mono-incineration)+17 (other thermal treatments including co-incineration)		32	25 (landscaping)	
Hungary	60	0.8		39		
Netherland		58 (mono-incineration + 27 (thermal dried)	15			
Norway	7			65	12	16
Slovenia	30	47 (export to incineration)	15	7		1
U.K.	1.5	19.5		67	5.2	1.8

It may be seen that in many countries agricultural utilisation still plays an important role while in others it was completely banned. Composting seems to increase its importance while more stabilized and sanitized sludge could be obtained by using this process, due to the intense stabilization and the process temperatures as high as 70°C. The application of thermal treatments is increasing as well as a result of progressively closure of the landfill disposal and agricultural use.

Table 2 [1]. shows the sludge production rate in different countries.

Table 2 Per capita sludge production (g/person × d) in different countries

Country	Sludge production (g/person × d)
Austria	55
Brazil	33
Canada	76
Italy	38
Finland	94
Hungary	48
Portugal	60
Slovenia	20
Turkey	60
Medium value	54

The sludge production range is quite large (20 – 94 g/person × d) thus indicating the different approach to WW treatment and sludge management in different countries. Sludge production depends more or less directly on the pollutants removal efficiency and chemicals added for phosphates precipitation and flocculation. Too high values, however, can indicate that the biological stabilization process is not completed. We can say that the appropriate values should be in the range of 45-65 g/(person × d), unless phosphorus removal process by chemical precipitation is performed.

In countries where technology is less developed, direct agricultural application or landfilling are the typical ways for secure sludge outlet from the urban WW treatment plants. In countries where land application was forbidden and where the landfill directive implementation into the national legislation was stringent, only high temperature destruction methods are available.

The Neptune project was addressed to discover new perspectives in sludge treatment which allow:

- a) to sustain agricultural utilization by producing a very clean and stabilized sludge;
- b) to set up new inertization processes so to overcome the problems linked to dioxins and furans formation during the conventional incineration;
- c) to develop a new approach to conventional incineration aimed to minimize the exhaust gas production and fuel consumption as well as improving phosphate recycling.

LEGISLATION

The most important European Directives to be taken into account for sludge management are:

- Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture;
- Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste;
- Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste;
- Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

The sludge included in the scope of the Directive 86/278 are only *residual sludge from sewage plants treating domestic or urban waste waters and from other sewage plants treating waste waters of a composition similar to domestic and urban waste waters*. It is therefore clear that only domestic sludge or urban and industrial **of similar composition** can be used in agriculture. Contaminated industrial sludge due the presence of organic and inorganic micropollutants at concentrations not expected in domestic sludge cannot be used in agriculture.

Limit values for metals in sludge (Table 3) and agricultural soil (Table 4) are included in the Directive.

Table 3 Limit values of heavy metal concentration in sludge used in agriculture (mg/kg dry solids)

Parameter	Limit values
Cd	20 - 40
Cu	1,000 – 1,750
Ni	300 - 400
Pb	750 – 1,200
Zn	2,500 – 4,000
Hg	16 - 25

<i>for</i>	Parameter	Limit values	<i>Table 4 Limit values of heavy metal concentration in soil sludge used in agriculture (mg/kg dry solids)</i>
	Cd	1 - 3	
	Cu	50 - 140	
	Ni	30 - 75	
	Pb	50 - 300	
	Zn	150 - 300	
	Hg	1 – 1.5	

Limit values are also fixed on annual quantities of heavy metals to be introduced in

the agricultural soil on a basis of 10 years (Table 5).

Table 5 Limit values of heavy metal application to agricultural soil ($\text{kg} \times \text{ha}^{-1} \times \text{year}^{-1}$)

Parameter	Limit values
Cd	0,15
Cu	12
Ni	3
Pb	15
Zn	30
Hg	0,1

It is worth to note that the document of the European Commission of April 2000 [2], which seems to be a draft of a new European Directive, includes new limit values for some organic micropollutants (Table 6). This proposal, anyway, never became a Directive.

The Directive 99/31 has set the standards for the landfill sites (of non hazardous, hazardous and inert waste) and the Council Decision of 19 December 2002 has established criteria and procedures of the acceptance of waste at landfill. In most of the cases the waste code of sewage sludge is 19 08 05 and it is classified as non hazardous waste. The base and sides of landfill site for non hazardous waste should consist of a mineral layer with thickness of at least 1 m and permeability lower than 1×10^{-9} m/s. Leachate and gas must be collected. No specific acceptance test is required for the non-hazardous waste to be disposed in non hazardous landfill sites unless it is disposed together with solidified and stabilized hazardous wastes. The directive requires that before landfilled the waste must be treated for reducing its quantity and the hazards to human health and the environment.

Table 6 Limit values for concentration of organic compounds and dioxins in sludge for use on land suggested in the document of the European Commission of April 2000 [2]

Organic compounds	Limit values
AOX1 (mg/kg dry solid)	500
LAS2 (mg/kg dry solid)	2,600
DEHP3 (mg/kg dry solid)	100
NPE4 (mg/kg dry solid)	50
PAH5 (mg/kg dry solid)	6
PCB6 (mg/kg dry solid)	0.8
PCDD/F7 (ng/kg dry solid)	100

¹ Sum of halogenated organic compounds.

² Linear alkylbenzene sulphonates.

³ Di(2-ethylhexyl)phthalate.

⁴ It comprises the substances nonylphenol and nonylphenoethoxylates with 1 or 2 ethoxy groups.

⁵ Sum of the following polycyclic aromatic hydrocarbons: acenaphthene, phenanthrene, fluorene,

flouranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1, 2, 3-c, d)pyrene.

⁶ Sum of the polychlorinated biphenyls components number 28, 52, 101, 118, 138, 153, 180.

⁷ Polychlorinated dibenzodioxins/ dibenzofuranes.

It should be pointed out that transposition of the above criteria and standards into national regulations were not homogeneous in Europe. In many countries limit values were set on organic carbon in the waste itself or in the leachate of percolation or leaching test. These limits practically hinder disposal of biodegradable waste, like sewage sludge.

The Directive 2000/76 establishes the general criteria for incineration and co-incineration. Co-incineration basically consists in the use of a waste for co-fuelling of an industrial apparatus used for energy or material production. The air emission values are reported in Table 7 for the incineration plants.

Incineration plants shall be operated in order to achieve a level of incineration such that TOC content of the slag and bottom ashes must be lower than 3 % or their loss on ignition lower than 5 % of the dry weight. Incineration and co-incineration plants shall be designed, equipped, built and operated in such a way that the gas resulting from the process is raised, after the last injection of combustion air to a temperature of 850 °C, as measured near the inner wall or at another representative point of the combustion chamber, for two seconds. Moreover, incineration and co-incineration plants shall have and operate an automatic system to prevent waste feed when temperature of 850°C is not reached or maintained or when the continuous measurements of the emission show that the limit values are not respected.

The limit values for co-incineration plants are calculated considering that a part of the exhaust gases is produced by the industrial plant using conventional fuels and a second part derives from the waste combustion. To this second part the same limit values of Table 7 are applied while limit values of the first part are fixed according to the type of industrial sector (generally they are much less stringent).

From this brief overview it results that the legislation on sludge disposal is evolving with specific regard to agricultural use considering that the directive is 24 years old. It might be supposed that in the next future only very good quality sludge will be admitted and probably new limit values will be included for organic micropollutants. Sludge usually contains nutrients, organic matter and trace elements, which are beneficial to the growth of crops (including energy crops and grass) and to the fertility, structure and/or texture of soils. They are therefore valued by farmers. It must also taken into account that sludges may contain contaminants, and/or pathogens, and may be odorous. Consequently, the whole process (from source control of potential pollutants, through sludge treatment, to sludge application and the way the land is farmed) should be controlled to avoid adverse impacts on the environment, or on plant, animal and human health. Such safe controlled use of sludge on land can be considered a component of future development [3].

Table 7 Air emission values (273°K, 101.3 kPa, 11% O₂ dry gas) of incineration plants

	Daily average value (mg/m ³)	Half hourly average value (mg/m ³)	
			97° percentile
Total dust	10	30	10
Gaseous and vaporous organic substances, expressed as total organic carbon	10	20	10
Hydrogen chloride (HCl)	10	60	10
Hydrogen fluoride (HF)	1	4	2
Sulphur dioxide (SO ₂)	50	200	50
Nitrogen monoxide (NO) and nitrogen dioxide (NO ₂) expressed as nitrogen dioxide for existing incineration plants with a nominal capacity exceeding 6 tonnes per hour or new incineration plants	200	400	200
	97° percentile of the daily average value over the year	All measurements in any 24 h period	95° percentile of all measurements determined as 10 minutes average
Carbon monoxide (CO)	50	100	150
	All average values over the sample period of a minimum of 30 minutes and a maximum of 8 hours		
Cd + Tl	0,05		
Hg	0,05		
Sb +As + Pb + Cr + Co + Cu + Mn + Ni + V	0,5		
	All average values over the sample period of a minimum of 6 hours and a maximum of 8 hours		
Dioxins and furans	0,1 (ng/m ³)		

SPECIFIC PROBLEMS AND PERSPECTIVES

From the legislation overview it results that in the coming years, large European wastewater treatment plants (WWTPs) will need to dispose of sludge by transforming it into inert material by thermal processes. In fact, sludge landfilling will be progressively restricted and agricultural utilization involving large amounts of sludge to be spread on land does not seem feasible for the following reasons:

- need of large extensions of fields and therefore long distances to be covered from WWTPs to the site of spreading;
- need of large storage volume required when sludge cannot be used (winter periods and when the fields are flooded);
- large WWTPs are often polluted by non-controlled industrial discharges that might hinder agricultural utilization of resulting sludge.
- A more sustainable sewage sludge management system might be therefore attained through a separation of primary and secondary sludge before their treatment and disposal. It would thus be possible to maintain agricultural utilization for biological sludge (secondary) and to convert to inert material by incinerating (on- or off-site) only the primary sludge [4].

In fact, characteristics of primary and secondary sludge are quite different in terms of quality (pollutants and nutrients) and in terms of suitability for thickening, digestion and dewatering. Secondary sludge is expected to be less polluted than primary sludge and should be segregated and treated separately from primary sludge, thus sustaining its agricultural utilisation.

Sludge separation may also give flexibility to sludge management, decreasing dependence on conventional disposal options (as required in the European Directive 2008/98), as sludge of good quality (biosolids) can be recovered for agricultural utilization while the remaining primary sludge can be treated by incineration. The challenge in the coming years will be assuring sludge management the greatest flexibility as well as maximizing the recovery of valuable products and energy sources while reducing disposal only to inert materials, which no longer contain useful compounds.

One of the main goals in secondary sludge processing is improving the performance of anaerobic digestion. Secondary sludge contains up to 70% of bacteria, so the above objective can only be achieved by accelerating the hydrolysis, which is the limiting step in the anaerobic process. Sludge disintegration treatments are able to disrupt biomass flocs and cell walls and to cause the release of the intracellular organic material. This treatment results in acceleration in the biological breakdown of particulate organic material into soluble, readily biodegradable fractions. The subsequent increase in biodegradable material improves bacterial kinetics, resulting in lower sludge quantities and, in the case of anaerobic digestion, increased biogas production. The technologies already in use for sludge disintegration, such as ultrasounds, by means of shear forces, have shown that energy input can account

for 1-2 kWh/kg TS [5],[6].

In this context, IRSA has carried out anaerobic digestion tests with sonicated secondary sludge, in batch and semi-continuous mode, investigating the effect of pre-treatment on digestion performances and on particle surface charge, affecting dewaterability. It is worth noting that ultrasound pre-treatment (specific energy 5,000 kJ/kg TS, i.e., about 1.4 kWh/kg TS) considerably accelerates the reaction rate (doubling the k values), and biogas production increases by about 30% with respect to the control reactor without sonication [7].

A second way to increase performance of secondary sludge anaerobic digestion is by thermal pre-treatment. The Cambi process may give even better results due to the drastic conditions of this disintegration process (temperature of 160 – 170 °C, pressure of 6 - 9 bar, residence time of more than 20 minutes). The Cambi process combined with anaerobic digestion allows increased VS removal and biogas production of 40 – 50 % in comparison with conventional sludge anaerobic digestion without disintegration.

Certainly, disintegration and digestion technologies of secondary sludge need to be optimised, taking into account both energy balance and sludge quality (reduction of volatile solids and pathogens, dewaterability).

COSTS OF SLUDGE PROCESSING

Costs are an important element for decision makers regarding sludge processing and outlet. They vary greatly depending on local conditions and on the size of the treatment facility. In order to achieve appropriate comparison of different choices of sludge treatment and disposal, it is important to take into account the overall annual costs, which are influenced by three main components. First, annual capital costs, depending on the sum to be invested, the method of financing, the depreciation period and the interest rates on borrowed capital. Second, running costs due to energy, chemicals, maintenance, salaries of the personnel, taxes, insurance. Third, the costs of disposal or recovery of the final product or residue. Table 8 shows some range of treatment costs [8].

Table 8 Range of sludge final treatment and disposal costs

Treatment and disposal system	Range of costs (€/dry t)
Utilisation in agriculture or forestry	90 – 240
Composting	150 – 360
Drying	180 – 480
Incineration	270 – 480
Landfilling	120 - 360

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IV. MERGING TECHNOLOGIES

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

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

Within the Neptune project, novel technologies were developed and further investigated, while regarding wastewater as a resource rather than a waste. These technologies comprise **bioelectrochemical systems** for energy recovery, denitrification and production of value-added products. Two new technologies were developed for the removal of micropollutant; **ferrate oxidation**, which can be used for the combined removal of pharmaceuticals and phosphate, and **biometals**, which permit both the chemical and biological removal of pharmaceuticals. **Co-metabolism during nitrification** was investigated as a possibility to optimize WWTP in terms of biological micropollutant removal, especially for the removal of residual estrogenicity. Phosphorus, and volatile solids recovery with **pyrolysis** and **biopolymer production** from sewage sludge are two techniques developed and tested for sludge revalorization.

Figure 1 visualizes how one or several novel technologies investigated in the Neptune project could fit in this WWTP of the future. The FeCl₃, normally dosed to the activated sludge system to precipitate PO₄³⁻, can be partially substituted by dosing a fraction of the iron as **Ferrate (Fe(VI))** in front of flocculation filtration to remove a wide range of highly persistent micropollutants together with phosphates. The application of **biometals** includes biogenic manganese oxides (BioMnOx) and biogenic palladium (BioPd) for the oxidative and reductive removal of pharmaceuticals and iodinated contrast media respectively.

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 or separate landfill storage for future recovery, due to the low content of heavy metals and no 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.

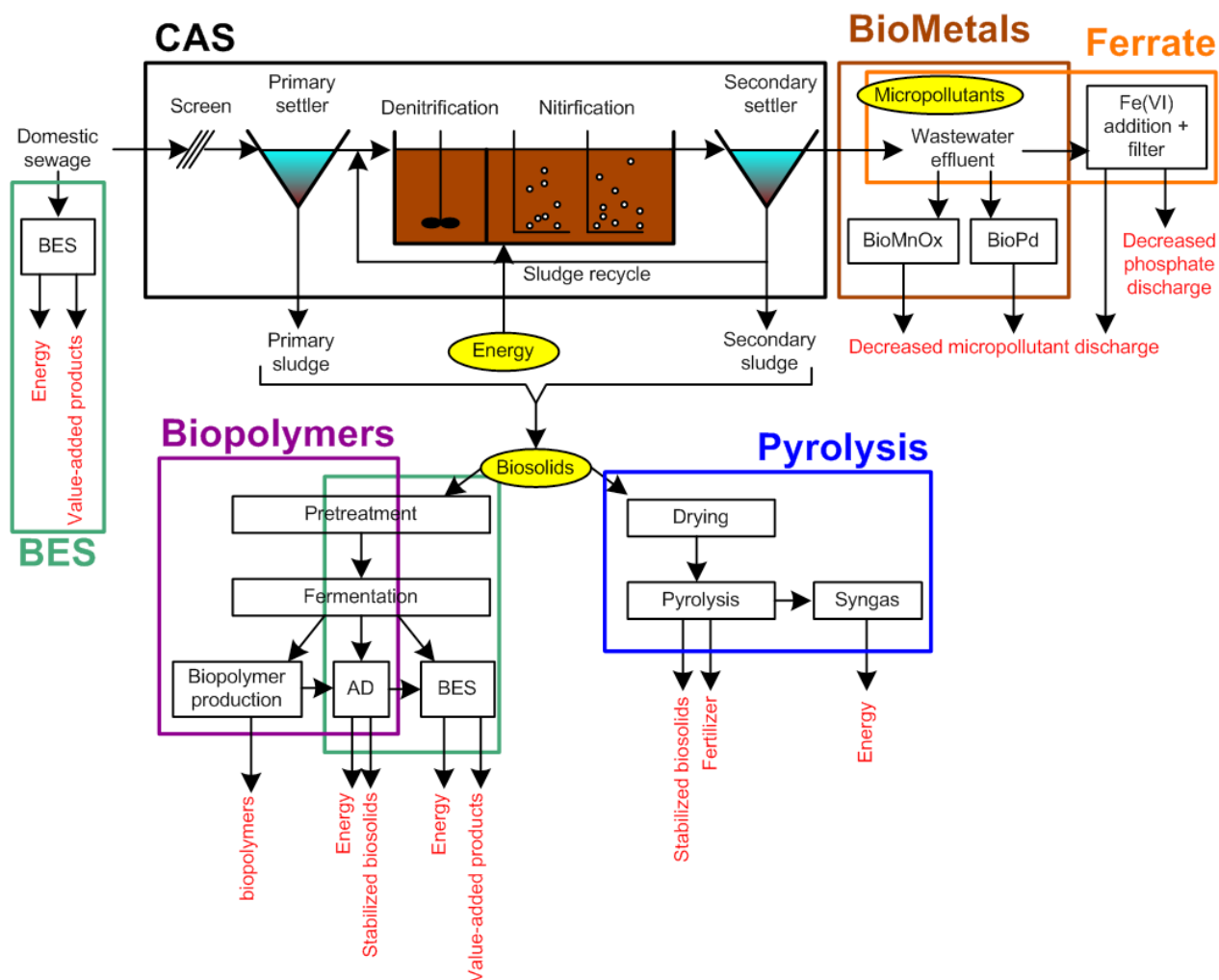


Figure 1 Overview of the novel technologies (Biopolymers, Bioelectrical systems (BES), Pyrolysis Ferrate, BioMetals with biogenic manganese oxides (BioMnOx) and biogenic palladium (BioPd), investigated in the Neptune project for the improvement of the sustainability of a conventional activated sludge (CAS) system.

V. FACT SHEETS

1

SLUDGE TRIAGE

1.1 INTRODUCTION

The volume of the sludge extracted from primary and secondary settling tanks is about 2% of the volume of treated WW. In spite of its negligible volume, sludge treatment and disposal entails very high capital and operating costs, which can be accounted as high as 50% of the total costs of the WW treatment plant, i.e. €25-35 / (person × year).

Although rich in nutrients, organic substance and microelements, in some countries sewage sludge is not accepted as agricultural fertilizer, due to the awareness regarding risks for contamination of typical products like milk, by the possible present toxic compounds. A good stabilization is a preliminary condition, both for sewage sludge agricultural use and landfill disposal. Anaerobic digestion was always considered the principal process to stabilize sewage sludge in the past years, at least for the large plants.

Separation of primary and secondary sludge processing could lead to more sustainable sludge management. Such an innovative concept is based on the following considerations: secondary sludge, poorer in pollutants than primary sludge, should be segregated and treated separately from primary sludge, to increase chances of secondary sludge utilisation in agriculture.

Due to the low water solubility and lipophilic properties of polycyclic aromatic hydrocarbons (PAHs), these compounds are typically removed from sewage by adsorption on the particulate material in the primary settling tank [1]. If such a primary sludge is blended with secondary it may render the mixed sludge no longer acceptable for agricultural use.

Secondary sludge, on the other hand, is much richer in nitrogen and phosphorus than primary sludge (5-8% instead of 1.5-5% of dry solids for nitrogen, and 1.6-6.0% instead of 0.3-1.5% for phosphorus), with consequent better profit for crops, which need smaller amounts of sludge to balance nutrient requirements.

Separation of primary and secondary sludge processing could also be advantageous from a technological point of view. Primary sludge in fact can be much easier thickened, digested and mechanically dewatered, as in a mixture with secondary sludge [2]. Moreover, primary sludge treatment can be more easily optimised for energy recovery and for the final incineration.

1.2 COLLECTION OF DATA OF PRIMARY AND SECONDARY SLUDGE QUALITY

Three WWTPs in the Rome area were selected for a monitoring campaign, with the aim to assess the pollution load and the nutrient contents of primary and secondary sludge. This monitoring campaign was specifically designed to verify whether the idea of sludge separation could be a solution to sustain the biological (secondary) sludge utilisation in the agriculture.

The three plants are Co.Bis. Cesano, 90,000 Population Equivalent (PE), Fregene 33,000 - 76,000 PE and Roma Nord 780,000 PE.

The total and volatile solids, and nutrient concentration of sludge of the three WWTPs are shown in Table 2. Metal concentrations are shown in Table 3.

Table 2 Solids and nutrient content of sludge of Rome North, Cobis and Fregene

		Total solids (g/L)	Volatile solids (g/L)	VS/TS (%)	Total P (% TS)	Total N (% TS)
Rome North	Primary	33.5-67.2	15.6-22.7	33.8-46.6	0.7-1.0	2.1-3.5
	Secondary	6.9-12.7	3.2-6.2	35.0-54.5	1.2-1.4	4.3-5.5
Cobis	Primary	9.1-11.8	6.2-8.7	66.5-74.6	0.2-1.4	3.2-4.6
	Secondary	5.0-5.3	3.4-3.9	68.1-72.4	0.5-3.5	4.9--8.6
Fregene	Primary	9.4-27.8	5.4-19.1	57.2-68.8	0.9-1.4	0.4-3.3
	Secondary	5.7-5.8	2.2-3.7	39.4-62.9	1.2-5.0	3.9-6.8

Table 3 Metals content (mg/kg DS) of sludge of Rome North and Cobis WWTPs

	Rome North		Cobis		Fregene	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
Cd	0.04-0.7	0.05-0.8	0.05-0.6	0.06-0.4	0.07	0.08
Hg	0.2-0.89	0.1-0.64	0.33-0.9	0.3-0.9	1.27	1.74
As	9.5-20	12.7-17	9.5-29	7.9-13	4	4
Ni	14-25	16.3-24	9.9-29	10.7-21	23	28
Cr	25.1+96	36.8-67	33-102	23.9-42	51	60
Pb	115.8-142	119.3-134	71-97	67-78.2	63	59
Cu	80.2-184	110.4-179	91.8-357	184-369	456	543
Mn	187.5+293	226.1+283	124-172	395.9-686	1220	1759
Zn	258.1-617	360.1-612	300.8-9.741	381.9-586	325	190

The average nutrient concentrations confirm that secondary sludge is richer in nitrogen (+60%, +130% and +170%) and phosphorus (+85%, +65% and +190%) than primary sludge. Volatile solid concentration of the Roma Nord sludges is quite low depending on the very prolonged sludge age and probably the inefficiency of the grit removal unit. No difference between primary and secondary sludge is found in heavy metals content. All values are far (1-3 order of magnitude) below the present European limits.

Figure 1 shows the concentration of organic micropollutant for both primary and secondary sludge sampled on the WWTPs of Roma Nord, Co.bis. and Fregene.

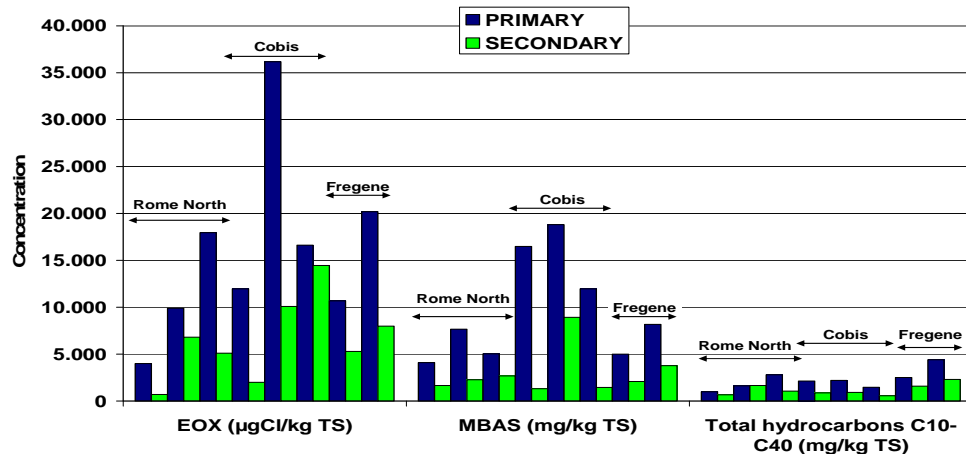


Figure 1 Organic micropollutant content of the sludges sampled on three WWTPs

Among numerous organic micropollutants extractable organic halogens (EOX), total hydrocarbons (C10-C40) and methyl blue active substances (MBAS), which are anionic surfactants, were chosen for monitoring. In fact, there are many contributors to the total amount of organic halogen

compounds in municipal wastewaters like detergents, disinfection byproducts, pesticides, varnishes, stain removers, flame retardants, cosmetics, pharmaceuticals, deodorants and many other halogenated solvents and synthetic materials consumed in handicraft activities and small industries connected to municipal sewers. WWTPs located in urban areas were much likely to receive wastewaters contaminated by hydrocarbons and PAHs from road traffic and phthalates from industrial activities. The origin of MBAS is typically the household detergents.

Figure 1 clearly shows that primary sludge is richer in organic micropollutant content than the secondary one. Instead, heavy metals, present in the tested sludge at very low concentrations, did not display any enrichment in primary or secondary sludge.

1.3 COMPARISON OF SLUDGE PROCESSING SCHEMES

The results of a sludge monitoring campaign pointed out that sludge management can be better accomplished by separate processing of primary and secondary sludge, especially in large plants. In fact, possibilities of sludge recovery for agricultural use could be impaired by the bad quality of primary sludge, when the two types of sludge (primary and secondary) are treated in mixture. In the large WWTPs the following further problems may be an obstacle to mixed sludge usage in agriculture:

- ⇒ large volume of cake requires large extensions of fields and therefore long distances have to be covered from the WWTPs to the site of spreading;
- ⇒ a large storage volume is required when sludge cannot be used (winter periods and when the fields are flooded);
- ⇒ influent WW of large cities are often polluted by non controlled industrial discharges that might impair agricultural utilisation of resulting sludge.

It must be pointed out that primary sludge can be easily treated by a conventional scheme including gravity thickening, anaerobic digestion, centrifugation and incineration while secondary sludge needs an intensive digestion process for accomplishing requirement of good stabilization (VS destruction > 40%). This can be achieved by sludge dynamic thickening and disintegration, either mechanical by ultrasound, thermal (T 170°C, θ 20 min) or chemical (alkaline or acidic) before digestion. This new sludge management scheme (Figure 2) was therefore compared to the conventional one (Figure 3) to highlight the main differences in term of energy balance and environmental emissions. For the incineration of primary or mixed sludge an integrated process was considered, including fluidised bed furnace and an indirect dryer where the steam produced in the heat recovery boiler downstream the furnace, is used. As an alternative to on-site incineration, on-site drying and off-site co-incineration (power plants or cement factories) as well as off-site incineration (in MSW incineration furnaces) were also considered.

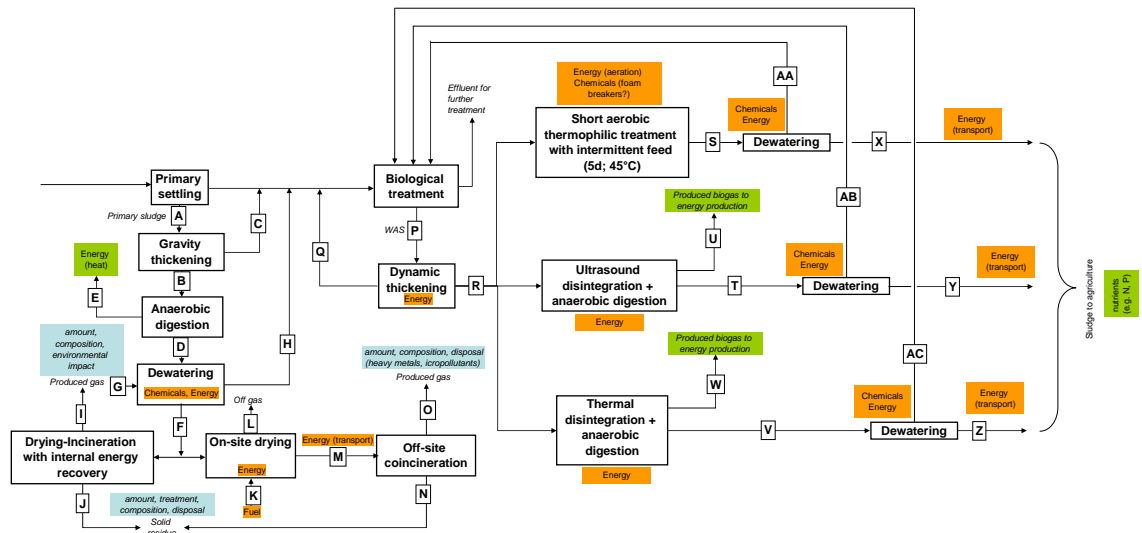


Figure 2 Proposed flow sheet with separate processing of primary and secondary sludge (green: energy production; orange: energy consumption)

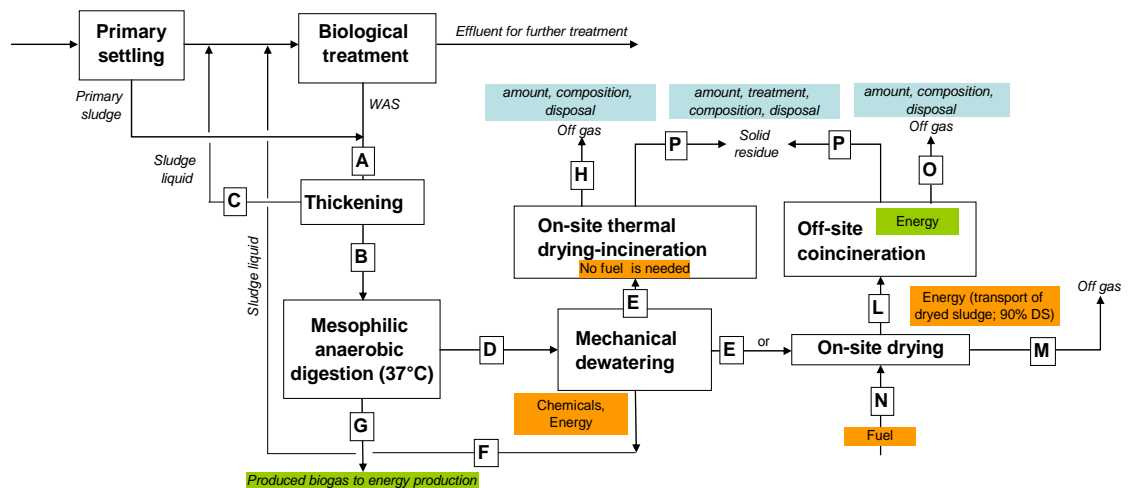


Figure 3 Conventional flow sheet of mixed sludge processing (green: energy production; orange: energy consumption)

For the flow sheet shown in Figure 2, total mass of primary sludge decreased from 3.97 (fresh primary sludge) to 0.36 kg/m³ WW (dewatered sludge) and to 0.103 kg/m³ WW (dried sludge), i.e. 91% and 97% reduction, respectively. Correspondingly, COD and VS are reduced 52% and SS 42%. Total mass of secondary sludge decreases from 12.3 to 1.54 kg/m³ WW (dynamic thickened sludge) and to 0.25-0.26 kg/m³ WW after thermal or mechanical disintegration, anaerobic digestion and dewatering and to 0.30 kg/m³ WW after short aerobic thermophilic treatment and dewatering, i.e. up to 98%. It is interesting to note that total mass of raw secondary sludge is more than 3 times higher than that of raw primary sludge, while the total dry solids of secondary sludge are only 75-80% of that of primary sludge.

Total mass of mixed sludge for the conventional flow sheet (Figure 3) is reduced from 16.2 (fresh mixed sludge) to 0.72 kg/m³ WW (dewatered sludge) and to 0.180 kg/m³ WW (dried sludge), i.e. 96% and 99% reduction. Correspondingly, COD and VS are reduced 52% and SS 43%.

Total output of dewatered sludge (primary + secondary) is therefore in the range 0.61-0.66 kg/m³ WW while the corresponding value of the mixed sludge is 0.72 kg/m³ WW (up to +18 and +9%, respectively).

The total production of off-gas from on-site incineration is estimated to be 1.12 Nm³/m³ WW (mixed sludge) and 0.598 Nm³/m³ WW (primary sludge). This means that incineration of sewage sludge is practically insignificant regarding environmental impact, at least considering the negligible exhaust gas production compared to the incineration of municipal solid waste. Moreover, it should be observed that production of mutagenic compounds like PCDD/F during sludge incineration (either primary or mixed) is not expected, considering that the chlorine presence in the sewage sludge is negligible.

When a direct contact dryer is used before the off-site disposal, a much more abundant gaseous effluent can be expected (7.54 and 3.63 Nm³/m³ WW for mixed and primary sludge, respectively). This is due to the great dilution required by the fresh air in order to keep the temperature of inlet gas to the dryer lower than 300 °C to avoid problems of combustion in the dryer and possible explosions due to the presence of fine particulates. Moreover, the humidity of exit gas from dryer should be kept quite low (generally lower than 0.1 kg H₂O/kg of dry gas) to guarantee that a sufficient gradient of water vapour is present in each section of dryer, for performing the operation with not so large equipment.

The subsequent incineration of dried sludge in an off-site plant would produce an additional exhaust gas of 1.353 (mixed sludge) and 0.789 Nm³/m³ WW (primary sludge). Total volume of exhaust gas from on-site drying and off-site incineration of dried sludge is therefore 8.9 (mixed sludge) and 4.42 Nm³/m³ WW (primary sludge), to be compared with the above figures of 1.12 (mixed sludge) and 0.598 (primary sludge) Nm³/m³ WW for an on-site drying and incineration. It clearly appears that on-site drying and off-site incineration of dried sludge is not a convenient option, also considering that a methane consumption of 71.7 (mixed sludge) and 34.4 L/m³ WW (primary sludge) is required for the thermal drying which represents 90 and 61.5% respectively, with respect to methane production in sludge digestion.

1.4 CONCLUSIONS

Primary and secondary sludge separate processing might be a good solution of sludge management for large WWTPs, where certainly many units for sludge thickening, digestion and dewatering are available for a separate treatment of the two kinds of sludge. The rationale of this approach is that it was proved that biological sludge (secondary sludge) is less polluted than primary sludge (at least with reference to hydrocarbons, EOX and MBAS) and more concentrated, with reference to nitrogen and phosphorus content. Its agricultural use might be therefore much more suitable than that of mixed sludge, as the worse quality of primary sludge can be detrimental. Moreover, it should be pointed out that the massive use of sludge produced in large plants is certainly a weak point of sludge management, due to the requirement of large volume for sludge storage during periods when agricultural use is not permitted by atmospheric and relevant field's conditions. The big distances to be covered for sludge transport for land application are another weak point.

This new strategy of sludge sorting represents the same policy used for the urban solid waste management (separate sorting of materials having different properties and compositions to increase opportunities for their recycling), and allows of:

- ⇒ reduced production of primary + secondary sludge compared to conventional treatment, considering that secondary sludge can be appropriately treated by dynamic thickening, disintegration and digestion, thus reducing considerably both the water content and the biodegradable solids;
- ⇒ reduced disposal problems only to primary sludge. To this purpose an integrated incineration process can be employed, thus minimizing the exhaust gas production to such low values (for a WWTP serving 500.000 PE 3.100 Nm³/h for primary sludge comparing to 5.800 Nm³/h for mixed sludge) that these type of plant can be considered like a pilot plant;
- ⇒ give more flexibility to sludge management considering that disposal of sludge is not accomplished by a unique solution.

Moreover, the study carried out in the Neptune project highlighted that sludge incineration should be preferentially performed by an on-site plant. The use of external incineration or co-incineration plants is not convenient, while the sludge has to be previously dried. In fact, the methane requirement for on-site thermal drying (34.4 and 71.7 L/m³ WW, for primary and mixed sludge respectively), if no other waste heat is available, would be subtracted from the amount to be recovered for electricity production, probably rendering not any more economical convenient energy conversion. Therefore, this option is not environmental friendly also considering the quite high amount of total gaseous effluent produced in drying and incineration.

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2

ULTRAHIGH TEMPERATURE PYROLYSIS

2.1 INTRODUCTION

Sewage sludge, a product of wastewater treatment, consists mainly of organic matter. Untreated it poses a potential risk for the health of people and animals and the damage of the environment. Before it is finally disposed off in any form, it has to be treated to minimise or eliminate the above risks. Ultra-high temperature pyrolysis is an alternative to sludge incineration which is nowadays most widely used in countries where sludge use in agriculture is prohibited. The first studies on sludge pyrolysis started 20 years ago. However, the research done so far included processes performed at temperatures only up to 800°C [1]; [2]; [3]. The fully operational sludge pyrolysis plant in Australia [4] runs at a temperature of 450°C. Process temperatures below 800°C result in three products: gas, an oily liquid as well as a solid residue (Figure 1).

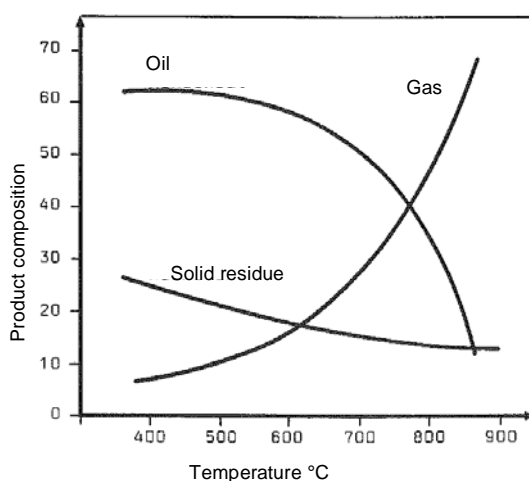


Figure 1 Distribution of sludge pyrolysis products depending on temperature

The PYROMEX ultra high temperature pyrolysis exposes the sludge to temperatures above 1250°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 results in the production of CO, H₂ and CH₄ (instead of CO₂ and

H₂O) so that the sludge energy content can be stored in another form than heat energy.

In addition, the higher process temperature is expected to eliminate the tar in the gas (no expensive gas cleaning) and to reach a complete degradation of organic micropollutants.

2.2 SCHEMATIC OUTLINE

Digested and dried sludge (TS>70%) is fed to the reactor through a pneumatic, electrically operated air-lock into a two stage storage tank where the material is de-oxygenated using inert gas. The de-oxygenated material is fed from the storage tank into the gasification chamber continuously by using a pneumatic, electrically operated air-lock via a screw conveyor. The basics of the process is sludge exposed to intense heat which is created by an induction coil wrapped around a specially developed tube that can withstand temperatures above 1700°C over a long period of time without corrosion. As a result, hydrocarbons are converted to a gas with a low content of CH₄ and a high content of CO. This corresponds to the composition of syngas, which contains 85% CO and H₂, with a smaller fraction of CO₂ and CH₄. The syngas can be used as an intermediate for the production of synthetic natural gas, chemicals, fertilizers, hydrogen, steam, transportation fuel or for electric power production. The obtained solid inorganic product could be safely disposed off since it is free of any hazardous micropollutants. In addition, the heavy metals content of the inorganic residue is lower compared to the one of the ash of incineration process due to the higher volatilization of the heavy metals and the remaining heavy metals are better immobilized, which was proved by the leaching experiments.

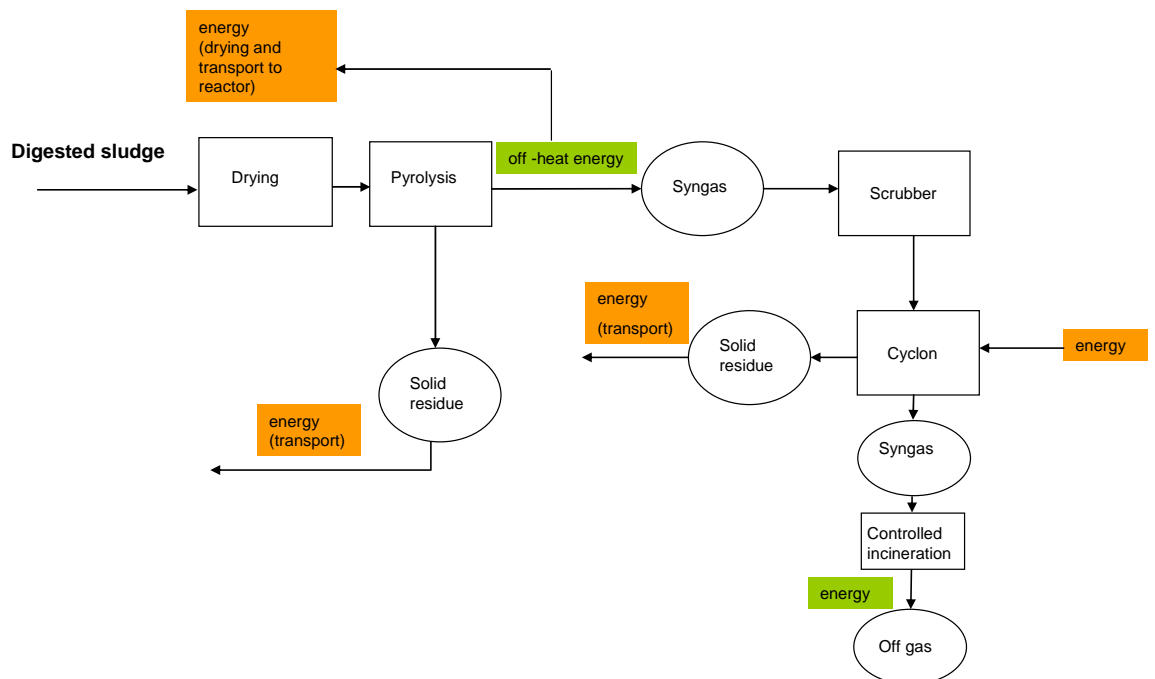


Figure 2 Schematic layout of the ultrahigh temperature pyrolysis process (green: energy production; orange: energy consumption)

2.3 SLUDGE QUALITY

The major process achievement is a reduction in TS content which increases at a higher temperature and residence time. Heavy metals content in the solid residue is below the limits set for fertilizers [5] and the phosphorus content is 6%-9%. In addition, heavy metals are well immobilized in the solid residue with less than 1.5% leached during the water leaching tests (material to water ratio was 1:20). These all together raises the potential for the usage as a fertiliser in agriculture in all countries where sludge application in agriculture is prohibited.

Table 1 Process outcomes

	<i>Reduction</i>
<i>TS content</i>	60-90% (depending on the process parameters)
<i>Organic matter content</i>	99.93% (from 75% to 0.05%)

2.4 PROCESS DESCRIPTION

2.4.1 Basic aspects

The sludge which enters the ultra-high temperature pyrolysis process could be either digested or raw sludge with a water content of up to 30%. The sludge is dried in a twin-line cascade drying system, whereby the sludge is fed into two cascade dryers operating simultaneously, in which the sludge is transported with augers through the heated pipe where the residence time should be in the range of 5-10 minutes. After the entrance where the temperature is approx. 600°C, optimum temperatures are reached in the range of 1000-1300°C (temperature is observed at three points: beginning, middle and end of the gasification tube). No chemicals are needed during the gasification process. The pilot plant (Figure 3) was mainly built to suit the purposes of the Neptune project.

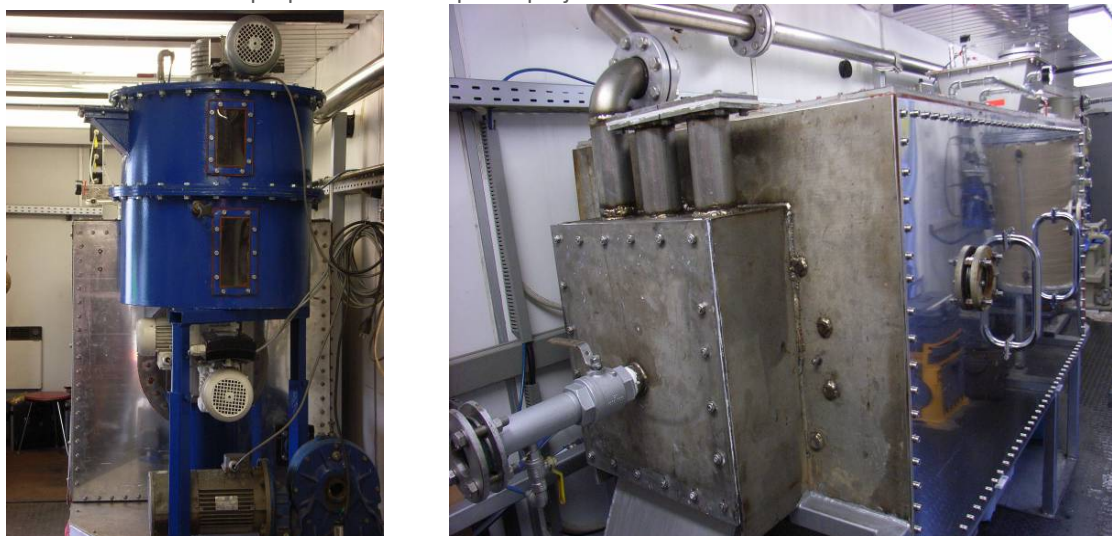


Figure 3 Pilot plant for ultra-high temperature gasification process with feed device (left) and

reactor tube (right)

Basic technical data is listed in the following table.

Table 2 Basic technical data of the pilot-scale plant

Gasification Unit	
Capacity:	1.2t/h per unit
Electricity consumption:	Approx. 20kW
Temperature:	1000°C-1300°C
Space requirement:	12mx3m
Total height:	2.5m
Weight:	2.6t
Gas Scrubber	
Throughput:	20m ³ /h
Foot print:	80m x 80m x 2m
Electricity requirements:	1.2kW

2.4.2 Equipment

Figure 2 shows the process layout including the following operations:

- Dewatering
- Drying
- Gasification
- Energy recovery, to be performed by different options such as:
 - Utilization of the syngas for sludge drying replacing oil and propane gas
 - Operation of a gas engine or gas turbine combined with a generator
 - Conversion of the syngas to hydrogen and production of electricity via fuel cells

2.4.3 Monitoring and control

The Pyromex system is monitored and controlled with a Siemens SIMATIC control system, which automatically monitors all parameters of the different operations: drying, feeding, gasification, scrubbing and gas utilization. Moreover, solid residue and syngas are also controlled. The risk of failure is minimized as the SIMATIC system immediately warns the operator when the slightest indication of a potential problem occurs. The entire system is computerized and a daily protocol can be printed out.

2.4.4 Maintenance - process stability – safety requirements

Maintenance and operation require one person per shift to be present on the plant. The maintenance costs are approximately 5% of the

investment costs as is common for any industrial machinery. Simple flushing of the gas train is required about once a week for cleaning purposes. Furthermore checking the scrubber residue should also be done approximately once a week. No other cleaning is necessary.

Start up and shutdown of the process is time consuming since couple of hours are needed to reach the process temperature and for cooling the reactor to ambient temperature respectively. However, the system is stable during the operation due to a lot of safety self-control points with the ability to switch off automatically whenever the safety is reduced:

- When an overheating condition is detected within the reactor, the induction heating is immediately decreased in an attempt to correct the situation. If monitoring detects a continued over-temperature condition, an immediate automated emergency shutdown procedure is initiated.
- Monitoring for avoidance of oxygen entering the reactor (should oxygen enter the chamber a fire would occur for a few seconds, however, this represents no risk.
- The reactor is operated under slight pressure. The reactor chamber contains a relief valve, set to open automatically at 2 bar. In case of blockage or other types of failure the relief valve will open to remove the gaseous fuels. These gaseous fuels are sucked via an emergency line into the afterburner.
- If the reactor is overfilled or a blockage of the reactor in-feed screw conveyor is detected by the control system, the in-feed conveyors automatically switch off. Since all screw conveyors are capable of operating both forward and reverse, it is possible to clear most blockages without disassembling the system.
- Cooling water pump failure. If a failure occurs with a cold water pump, it is detected by the control system and the redundant pump is switched on. Therefore, it is not necessary to stop the system.

2.5 Costs

The costs are presented as follows:

- Investment costs of a 25t/day unit complete with dryer and energy production 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 when the dryer is fed with the material at about 6-12% solids.
- Personnel costs are €200'000/year (4 people are required for operation and maintenance)
- Energy balance for 1t dry solids is as follows, with the remark that any energy recovery from the evaporated water or energy savings due to the use of solar energy will have big impact on the total balance.
- No chemicals or any additives are needed

	Electricity	Heat
Consumption	1'200MJ or 330kWh	5'300÷7'000MJ (drying from 25-30% to 70%)
Production from syngas	3'000MJ or 850kWh	4'500MJ
Net production	1800MJ or 500kWh	-800 ÷ -3'200MJ

2.6 FULL SCALE EXPERIENCE

An industrial 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 full-scale operation experience. Both plants have been dismantled and the first commercial plant is under construction in Eitting, Germany.

2.7 KNOWLEDGE GAPS

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.

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3

SEPARATE HOSPITAL WASTEWATER TREATMENT

3.1 INTRODUCTION

Hospital wastewater contributes to the load of pharmaceuticals in the environment. To evaluate the significance of hospitals in general or of a specific hospital in the catchment of a particular sewage treatment plant, mass fluxes must be analyzed to compare the pharmaceutical loads from hospitals with the ones originating from patients at home.

It is well known that with conventional activated sludge treatment many pharmaceuticals cannot be eliminated from wastewater and reach ambient waters. In order to reduce the load of pharmaceuticals in the environment, the following strategies are in discussion: upgrading the municipal wastewater treatment plants with advanced treatment steps like ozonation or addition of powder activated carbon (PAC), separate treatment of hospital wastewater and source control measures (e.g. ecolabeling of pharmaceuticals). Concepts for the separate hospital wastewater treatment are discussed in this fact sheet.

3.2 MASS FLUXES

Information on consumption of pharmaceuticals in hospitals is not easily available. In Switzerland, IMS Health is providing sales data from pharmacies, drug stores, doctor's practices and hospitals. According to this statistics 18% of the hundred pharmaceuticals used in the highest quantities are dispensed by hospitals [1].

The contribution of pharmaceuticals from hospitals was calculated for a general hospital in Switzerland (see Table 1 for details). In 2007, 1'154 kg of pharmaceuticals were administered to patients in the hospital. 779 kg are excreted in unchanged form as parent compounds [2]. 57% of this amount stemmed from contrast media, 19% from laxatives, 16% from antibiotics, and 8% from others. This hospital is discharging to a wastewater treatment plant (WWTP) with 54'000 inhabitants, resulting in a hospital bed density of 6.3 beds per 1'000 inhabitants. Based on data from IMS health of the top-40 pharmaceuticals sold in pharmacies, drug stores, and

doctor's practices in 2004, a total of 1'267 kg per year was calculated to be excreted from households as parent compound into the WWTP. Thus, around 38% of the pharmaceuticals at the wastewater treatment plant in this case study stem from the hospital.

For these calculations no excretion of patients going home are considered. Mass flows of X-ray contrast media and cytostatics were analyzed in the wastewater of another Swiss hospital [1]. Measured loads over one week were compared to the actual consumed amounts during the sampling period. The results showed that hospitals are indeed a point source for X-ray contrast media. 50% of the administered amount was recovered in the hospital sewer, the rest is most probably excreted into domestic wastewater by the patients treated at the hospital but who went home after the treatment. These so called out-patients account for about 50% of all patients. The cytostatics 5-fluorouracil, gemcitabine and 2',2'-difluorodeoxyuridine (the main metabolite of gemcitabine) were also found in the hospital sewer, however, only between 1.1 and 5.5%. About 70% of the total quantity of cytostatics was administered to out-patients, which is a plausible explanation for the small recoveries in the hospital wastewater. So, to come back to the general hospital from before (details in Table 1), we can assume that also around 50% of the contrast media are taken home by out-patients. Taking this into account, the contribution of pharmaceuticals from the hospital at the wastewater treatment plant is not 38% but around 30%.

A detailed mass flow analysis was done at Caboolture Public Hospital in Queensland, Australia, discharging its wastewater to a WWTP with around 45'000 inhabitants [3]. Approximately 200 hospital beds result in a hospital bed density of 4.4 beds per 1000 inhabitants. Samples of hospital and municipal wastewater were analyzed for 59 substances. For 28 of 30 quantifiable compounds, less than 15% of the pharmaceutical residue loads originated from the hospital. However, in this study contrast media were not included in the mass flow analyses.

Beside the hospital, also a psychiatric center in Switzerland was evaluated for the mass flow of pharmaceuticals (Table 1). In 2007, 52 kg of pharmaceuticals were consumed in the psychiatric hospital, of which 17 kg were excreted [2]. The main fraction came from laxatives with 36%, followed by analgesics/antiphlogistics 17%, antidiabetics 15%, psychotropic pharmaceuticals 11%, and others 21%. This shows that the mass fluxes are not only compound specific but also site specific.

Currently a model is established, based on a urban substance flow model developed earlier [4], to provide mass flows of pharmaceuticals from hospitals and to localize hotspots in the Swiss surface water network. The information gained in this study regarding input loads of pharmaceuticals from hospitals enables the risk assessment of these point sources, as required for deciding whether dedicated treatment of hospital effluents is advantageous for urban water management.

3.3 ABSTRACT

To eliminate pharmaceuticals in hospital wastewater, four concepts can be envisaged:

- No-mix toilets. In such toilets the urine is collected and treated separately.
- Vacuum toilets. All excretions are collected in a tank with low dilution. This waste is directly incinerated.
- Source separation by collecting urine with bottles or roadbags. Part of the urine is already collected by the means of catheters. An additional collection could be done for patients who are treated with contrast media. The collected urine is incinerated.
- Decentralized treatment of hospital wastewater. Biological treatment (e.g. with a membrane bioreactor) with an advance post-treatment (e.g. with ozone, PAC) is possible. Such post-treatment is necessary for the elimination of pharmaceuticals. Ozonation is very efficient for most pharmaceuticals. For X-ray contrast media, an additional step is necessary, e.g. advanced oxidation processes with ozone/H₂O₂. Alternatively activated carbon may be used as post-treatment.

To be able to compare these concepts, cost calculations are necessary (see 1.4).

3.4 COSTS

Costs were calculated for the following concepts to be able to make comparison.

- Decentralized treatment of hospital wastewater.
 - Pre-treatment: membrane bioreactor MBR (with a screen and a fine screen)
 - Post-treatment: ozonation (10 mg/L ozone)
 - PAC (20 mg/L)
- Vacuum toilets and wastewater incineration.
- Direct treatment of urine by ozonation (1'000 mg/L ozone).
- Direct treatment of urine by PAC (2'000 mg/L).
- Source separation by collecting urine with bottles or roadbags from patients being treated with contrast media (stationary and out-patients). The collected urine is incinerated with the household waste.

Two medical institutions were evaluated: a general hospital and a psychiatric center (see Table 1 for details). The hospital has the advantage of an already existing building for the wastewater treatment. At the psychiatric center, a new building must be constructed. Therefore investment costs at the psychiatric center are higher than those at the hospital. The basis of the cost calculation are in Table 1.

Table 1 Parameters of the two analyzed medical institutions.

Parameter	Units	Hospital	Psychiatry Center
number of hospital beds ¹	[beds]	371	211
sewage flow ¹	[m ³ /y]	116,000	23,250
urine and flushing water in no-mix toilets ²	[m ³ /y]	429	225
anyway collected urine (e.g. catheters, waterless urinals) ²	[m ³ /y]	68	12
urin. faces and flushing water in vacuum toilets ²	[m ³ /y]		804
		1,533	
urine in urine bags (stationary) ²	[m ³ /y]	3.75	-
urine in urine bags (stationary and ambulant) ²	[m ³ /y]	10.4	-

¹ measured values

² calculated values based on assumptions

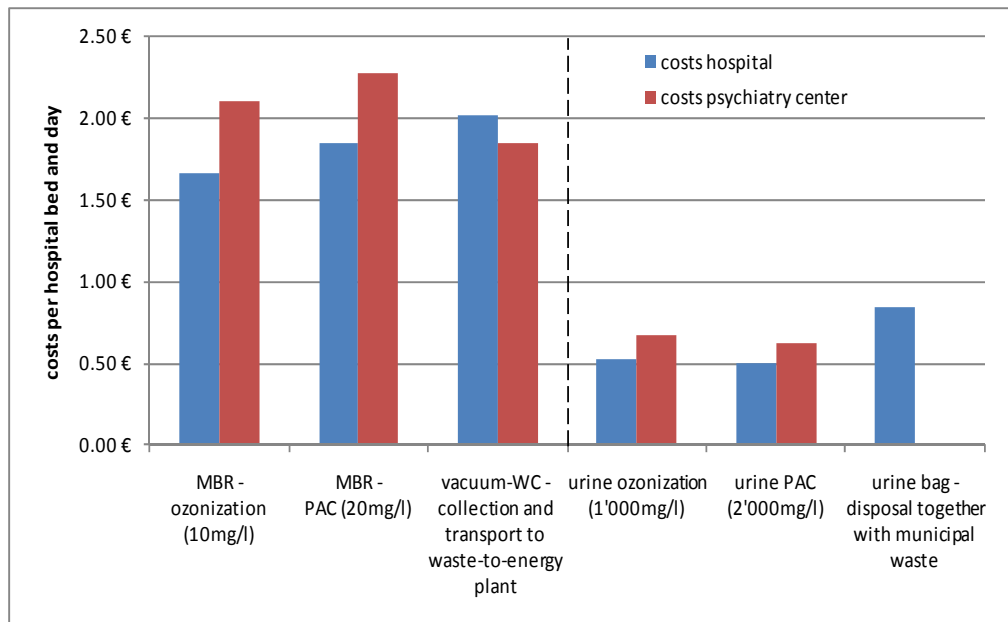


Figure 1 Costs per hospital bed and day for the six analyzed options. The first three options (left of the dashed line) account for the whole wastewater stream. The second three options (right of the dashed line) account for urine only.

Table 2 Costs of different concepts at the hospital and psychiatric center.

		screen - fine screen - ozonation MBR (10mg/l)	screen - fine screen MBR - PAC (20mg/l)	vacuum-WC - collection and transport to waste-to-energy plant	urine ozonation (1'000mg/l)	urine PAC (2'000mg/l)	urine bag - disposal together with municipal waste
costs hospital	capital costs	€1'520'000	€1'780'000	€1'170'000	€620'000	€640'000	€0
	operating costs	€90'000	€90'000	€170'000	€20'000	€10'000	€110'000
	annual costs	€220'000	€250'000	€270'000	€70'000	€70'000	€110'000
	costs per hospital bed and day	€1.64	€1.83	€2.02	€0.53	€0.49	€0.46 ² € 0.84
	costs per m ³ wastewater ¹	€1.90	€2.16	€2.33	€0.60	€0.60	€0.95
costs psychiatric center	capital costs	€1'360'000	€1'490'000	€570'000	€460'000	€470'000	-
	operating costs	€40'000	€40'000	€90'000	€10'000	€10'000	-
	annual costs	€160'000	€170'000	€140'000	€50'000	€50'000	-
	costs per hospital bed and day	€2.10	€2.26	€1.84	€0.67	€0.63	-
	costs per m ³ wastewater ¹	€6.88	€7.31	€6.02	€2.15	€2.15	-

¹ The costs per m³ wastewater are calculated by dividing the annual costs by the annual wastewater amount.

² only stationary patients

3.5 CONCLUSIONS

The mass flux studies show that the load of pharmaceuticals coming from hospitals are compound specific (contrast media show the highest loads in a general hospital) but also site specific as e.g. psychiatric clinics are using much smaller amounts of pharmaceuticals. Hospitals contribute to a significant extent to the total urban wastewater load for contrast media and to a lesser extent for laxatives and antibiotics. Taking into account that around 50% of the contrast media consumed at the general hospital are taken home by out-patients, the contribution of pharmaceuticals from the investigated general hospital at the wastewater treatment plant is around 30%. Other studies at different sites show lower contributing amounts of hospitals.

As the Table 2 and Figure1 show, costs are highly depending on already existing infrastructure. Infrastructure already exists in the analyzed hospital. Therefore the costs are lower for all options except the introduction of vacuum-toilets. This is due to the fact that the option of vacuum-toilet does not need an additional building.

The first three options in Table 2 are meant to process the whole wastewater stream, whilst the second three options only account for the urine part of it. Due to the fact that urine bags account for stationary as well as out-patients it is recommended to treat urine with urine bags. If urine bags will be used only for stationary patients the costs per hospital bed and day decrease to €0.46, which is less than the other two urine only treatment options.

64% of all pharmaceutical residues are excreted in urine [5]. This relatively small fraction of urinary excreted substances does not speak for separate treatment of urine.

In Switzerland, municipal wastewater treatment costs about €1.33 per m³ wastewater (median), and with an additional treatment with ozone or PAC around €1.6 per m³. The costs per m³ for the hospital wastewater treatment concepts in Table 2 are in the same range as for those concepts which treat the whole wastewater stream at the central treatment plant. The concept costs for the psychiatric center are significantly higher. The costs per m³ wastewater for the concepts which only account for the urine fraction are lower, but those concepts do not treat the whole wastewater stream, therefore those values are not comparable.

Benefits and limitations of the analyzed concepts are shown in Table 3.

Table 3 Benefits and limitations of the analyzed concepts.

Concept	Benefit	Limitation
screen - fine screen - MBR - ozonation (10mg/l)	<ul style="list-style-type: none"> • Most substances are oxidized. 	<ul style="list-style-type: none"> • The substances are transformed, not removed. • High energy demand.
screen - fine screen - MBR - PAC (20mg/l)	<ul style="list-style-type: none"> • Most substances are removed. • removal of substances (not just transformation). 	<ul style="list-style-type: none"> • PAC must be disposed. • High energy consumption in PAC production.
vacuum-toilets - collection and transport to waste-to-energy plant	<ul style="list-style-type: none"> • Most of the excrements do not get into the sewer system but are collected. 	<ul style="list-style-type: none"> • The installation of vacuum toilets is complex and reasonable only in terms of a reconstruction or new construction. • The vacuum sludge must be combusted which is energy demanding because TSS is very low < 1%.
urine ozonation (1'000mg/l)	<ul style="list-style-type: none"> • Substances contained in urine are oxidized. 	<ul style="list-style-type: none"> • Energy demanding. • Only a small fraction of sub-stances are excreted via urine.
urine PAC (2'000mg/l)	<ul style="list-style-type: none"> • Substances contained in urine are absorbed. 	<ul style="list-style-type: none"> • Only a small fraction of sub-stances are excreted via urine.
urine bag - disposal together with municipal waste	<ul style="list-style-type: none"> • Substances contained in urine are separated from the wastewater stream. • Low costs compared to the other concepts 	<ul style="list-style-type: none"> • Only a small fraction of sub-stances are excreted via urine. • Only reasonable concept for contrast media.

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4

WET OXIDATION

4.1 INTRODUCTION

Nowadays wastewater urban sludge treatment is a challenge with a constant demand for nutrients and micropollutants removal improvements, while at the same time the energy consumption is expected to decrease or even result in the energy gain. Wet oxidation sludge treatment process belongs to the new technologies for the final treatment of the digested sludge and is an alternative to the sludge incineration.

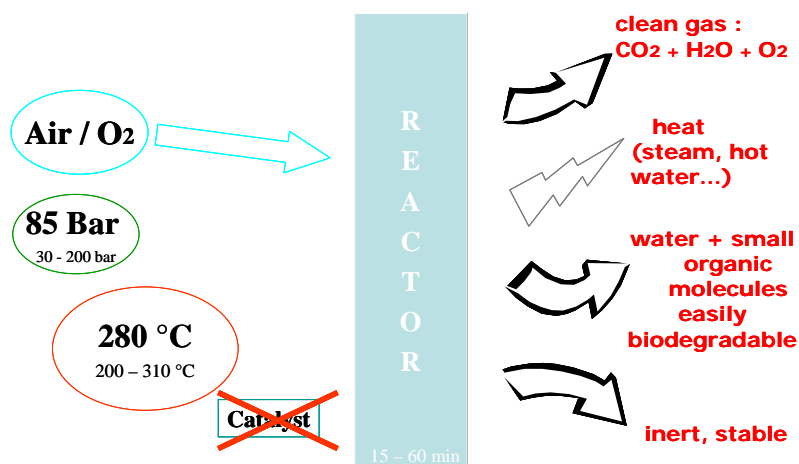


Figure 1 Basic principles of the WO process

Wet oxidation is a reaction in the liquid phase between organics and oxygen at elevated temperature and pressure. It could be used for different kind of industrial and urban effluents which contain high amounts of organic compounds. The basic chemical reaction is as follows:



Orbe was the first European community to apply non-catalytic WO process for the municipal sludge treatment in 2001. Since then the process has been further optimised and at the moment is more economical solution than incineration for the

4.2 SCHEMATIC OUTLINE

Compressed air or pure oxygen is mixed with sludge and the mixture is preheated in the heat exchanger, by using the heat of the liquid after reaction. The WO reaction occurs in a vertical tubular reactor, which operates as a pressurised bubble column. The temperature of the medium will increase in the reactor since the WO is an exothermal process.

If the organic content of the sludge is high, the excess heat can be used for the industrial steam or hot water production. After the recovery of excess heat, the fluid is used to preheat the incoming liquid. After cooling, the liquid/gas mixture is separated in a phase separator and decompressed using regulation valves. The gas phase is composed mainly of CO₂ and excess of O₂, but it may contain traces of CO and volatile organic carbon (VOC). The schematic outline of the process is given in Figure 2.

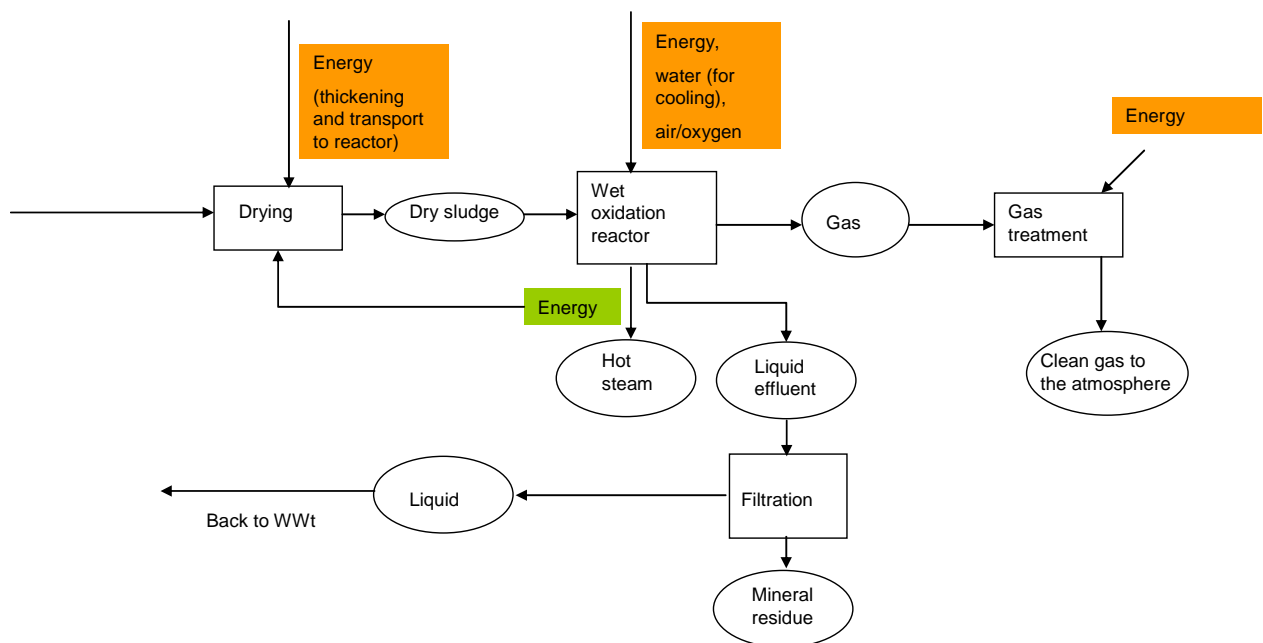


Figure 2 Schematic layout of wet oxidation process (green: energy production; orange: energy consumption)

4.3 SLUDGE QUALITY

The major process achievement is stable mineral solid product with less than 3% content of TOC. The mineralisation of organic matter is not complete (75%); however, the COD returned to the digester is easily biodegradable and enhances the methane production. High content of phosphorus in the mineral residue (8%), of which almost 9% is bioavailable, offers possibilities for phosphorus reuse.

Table 1 Process outcomes

	Reduction
Organic matter total (solid and liquid)	75%
Organic matter content in the solid product	97%

4.4 PROCESS DESCRIPTION

4.4.1 Basic aspects

The sludge which enters the process could be either digested or raw sludge with a water content of more than 85%. The feasibility of the treatment is determined by the concentration of organic compounds, which should be in the range of 70-120kg/m³ COD. The residence time should be in the range of 30-60 minutes. Optimal temperature is from 250-300°C and pressure is in the range of 60-100 bar.

Table 2 Basic data of the WO plant

Wet oxidation unit (average data for year 2006)	
Capacity:	12m ³ /d
TS:	9.80%
COD:	99g/L
Electricity consumption:	420kWh/d
Oxygen consumption:	1050kgO ₂ /d
Oxidized liquid out (to the digester):	11.1m ³ /d
Solid mineral out:	880kg/d
Gas out (to the atmosphere):	1080kg/d
Space requirements:	
Total height:	
Weight:	
Operator:	0.5men/yr
Maintenance:	25d/yr
Excess heat recovered:	
Hot water:	3 GJ/d
Heat:	1.1 GJ/d

4.4.2 Equipment

Figure 2 explains the process layout with the following parameters:

- Effluent preparation unit
 - In case of digested sludge treatment the optimal consistence of sludge for the WO treatment is comprised between 10 and 15% dry solids. In case of sludge from aerobic treatment , the optimal dry solid concentration is lower; 5-10%. This is achieved by using dewatering drum or centrifuge. A buffer tank must be included as well to ensure the sludge homogeneity.
- Wet oxidation unit
 - High pressure pump
 - heat recovery exchanger
 - reactor
 - heat storage exchanger
 - liquid-gas separator

- Mineral residue separation unit
 - The liquid after WO treatment contains a mineral residue which has to be separated by a press filter or rotating filter. The filtered liquid contains only easily biodegradable compounds and can be returned into the biological wastewater treatment line. The mineral residue dewatered in a filter contains 55-80% dry matter and might be used for road construction or for the brick production provided that the authorities authorize it and recognize such product as secondary raw material rather than as a waste.

4.4.3 Monitoring and control

The oxidation process is entirely automatic with constant self control and besides the start up periods does not need a constant presence of an operator which results in a 0.5men/year requirement. This includes regular measurements (once per week) of the following parameters: COD abatement control, volatile organics content in the solids leaving the reactor, total solids content of the inlet and outlet of the reactor, as well as visual control of the pipes and valves once per day. The inlet and outlet gas and liquid flow rates, as well as the oxygen concentration in exhaust gas are continuously monitored and automatically adjusted by regulation loops.

4.4.4 Maintenance - process stability – safety requirements

Operation requires 0.5 person to be present at the plant 5 days/week. The operator work includes the supervision and routine manipulations, troubleshooting and stock control (spare parts). Additionally, a stand-by duty is necessary and it represents the charge of work of 0.25 persons. The maintenance costs are approximately 3.5% of the investment costs which takes into account the spare parts and external reparations. Automatic drain system of the reactor and automatic online washing of high temperature tubing in order to eliminate the eventual deposits is included in operation. The detailed control and cleaning of the equipment is performed during the maintenance periods (2x year) which requires 1 person during 2 weeks (or 2 persons during 1 week). Start up and shutdown of the process require about 4 to 8 hours of the operator presence. The system is stable during the operation due to a lot of operation self-control loops. In case of fail of an element, the excessive variation of operating parameters (temperature, pressure, flow rates or levels) activates the safety system which sends an adequate alarm on the stand-by duty phone or, depending on the alarm type, immediately stops the installation. In any case, if no intervention of the operator occurs during a fixed delay, the safety system stops the installation. In many cases, the troubleshooting may be easily performed on distance, through the supervision screen. Therefore, the intervention on site during the week-end or during the night may be avoided.

4.5 COSTS

Both investment and the operating costs are strongly dependent on the size of the plant. As presented in the Figure 3 operating costs vary from more than €300 /t DS treated, for a plant serving a population less than 10'000 equivalents inhabitants (EI), to €200 /t DS treated for a plant serving 1 mil EI. The ratio is even higher if the interest is taken into account.

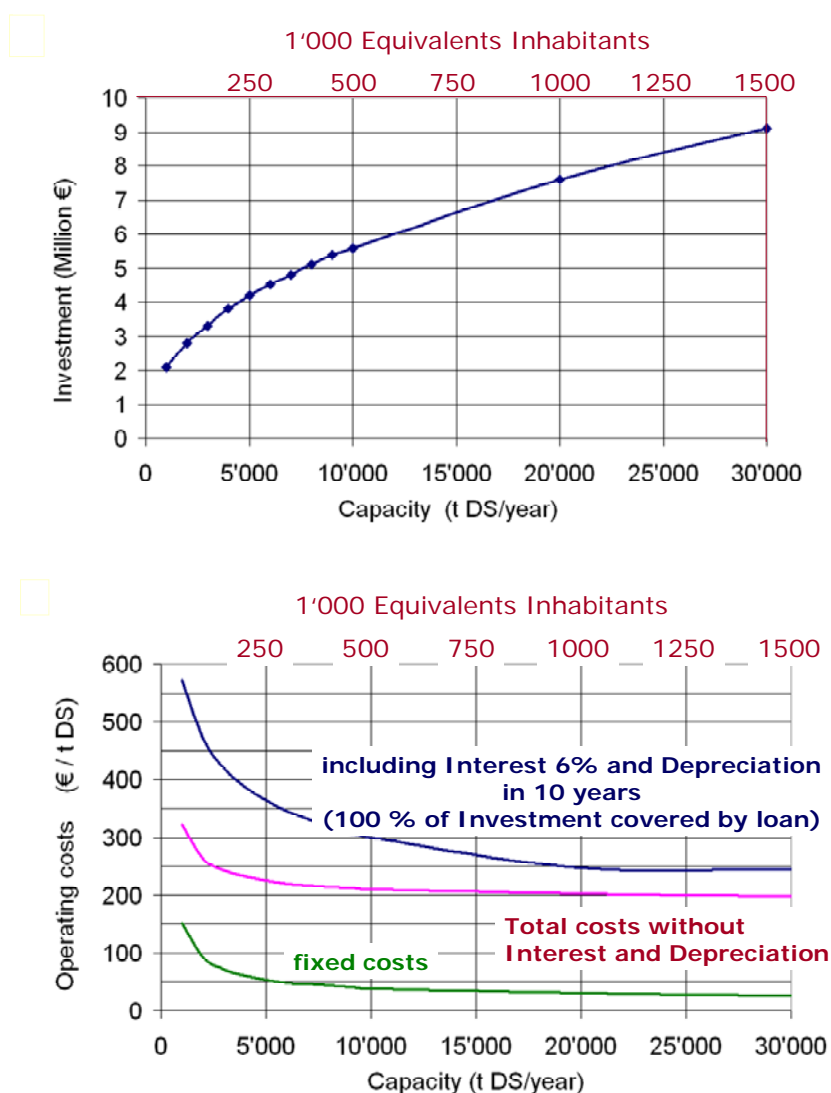


Figure 3 Dependence of the investment and operating costs on the plant size

4.6 FULL SCALE EXPERIENCE

Industrial size plant with a capacity of 12 m³/d treating sludge has been operated in Orbe, Switzerland (Figure 4) since 2005. To treat the whole amount of sludge produced in Orbe, the unit operated 24h/day, 260days/year.



Figure 4 Wet oxidation plant, Orbe, Switzerland

4.7 KNOWLEDGE GAPS

The further possible improvements of the process are related to the diminishing the electrical energy consumption (use of energy efficient pumps and other electric elements); also, valorisation of solid residue has to be fully assessed and validated by the competent authorities.

5

THERMAL HYDROLYSIS

5.1 INTRODUCTION

Thermal hydrolysis is a process used to increase performance of subsequent anaerobic digestion of activated and primary sewage sludges. During thermal treatment, sludge is heated at high temperature and pressure for a defined period (normally approx. 15 minutes in total). Microbial cell walls in the sludge are destroyed, releasing more easily digestible organic compounds contained within the cells. The advantages of combining thermal hydrolysis and anaerobic digestion are high volatile solids (VS) destruction and increased biogas production. Currently, the most known commercial thermal hydrolysis technologies are Cambi® and BioThelys®.

In the 1990's thermal hydrolysis was evaluated in Norway, and was developed into a viable technology that has received considerable attention in Europe, primarily through the efforts of Cambi, a company that grew out of the research in Norway. The Cambi technology has been applied in 17 plants worldwide and has been in operation for 13 years.

The Cambi process is a batch process, consisting of three high pressure, high temperature hydrolysis tanks. Continuous thermal hydrolysis systems are still in the early stages of development. This technology may be retrofitted ahead of existing digesters, or may be incorporated into new facilities. Compared to competing sludge pre-treatment technologies, key advantages are high performance (VS destruction and gas production), ability to feed at high solids concentrations (approx. 10%), improvement of biosolids dewaterability, and total pathogen destruction. Disadvantages are higher technological requirements (i.e., the need to operate a steam boiler), generation of coloured soluble inerts, and poorer solids capture.

5.2 SCHEMATIC OUTLINE OF CAMBI THP

The hydrolysis process consists of three pressure vessels, with the entire digestion process consisting of 1. Pre-dewatering to approx. 10%, 2. heating to approx. 3 bar (130°C), 3. heating to 5-6 bar (150°C-160°C), 4. flashing to 3 bar, 5. cooling to digestion temperature, 6. biological anaerobic digestion, and 7. final dewatering. Units are summarised below the figure.

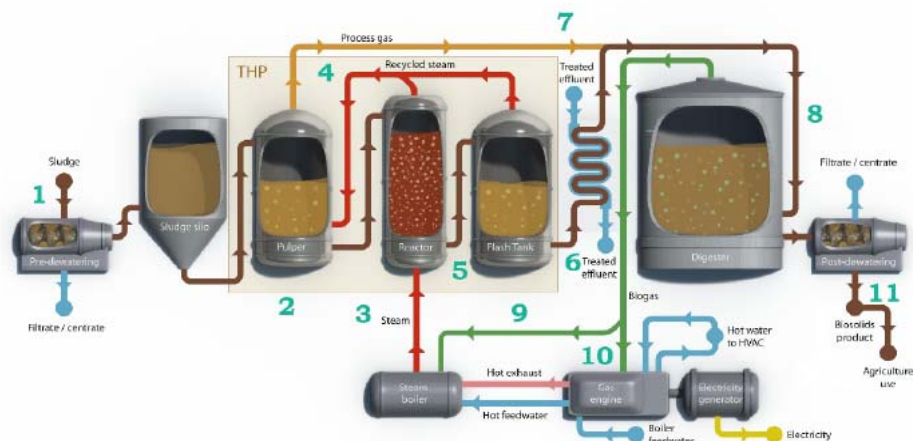


Figure1 showing 1. Decanter, dewatering unit, 2. Pulper, pre-heating vessel, 3. Reactor, pressurised sludge vessel, 4. Recycled steam, 5. Flash tank, de-pressurise vessel, 6. Heat exchanger, 7. Foul gas, 8. Digester, 9. Biogas for steam generator, 10. Biogas for gas engine, 11. Decanter, dewatering unit

5.3 EFFECT ON SLUDGE CHARACTERISTICS

Cambi normally states VS destruction higher than 50%, with improved sludge dewaterability in excess of 50%. In addition, due to an increase in feed solids, the digester can be better utilised, with decreased hydraulic retention times, routinely at 12 days retention time and organic loading of 6.5 kg VS/m³/day . Cambi provides guarantees as shown in the following table:

Table 1

Guarantee		Conditions	
COD conversion	COD/VS	HRT	Dig Temp
56%	>1.7	>18 days	38-41°C
54%	1.6-1.7	>18 days	38-41°C
52%	1.5-1.6	>18 days	38-41°C

The process has been extensively analyzed as part of the Neptune project, and with an activated sludge stream, Cambi's claims have been largely verified, with an additional dependence on upstream sludge age as shown in the figure. This demonstrates that in most cases, approximately 60% degradability (55% VS destruction) can be expected, but that performance may drop at very high sludge ages.

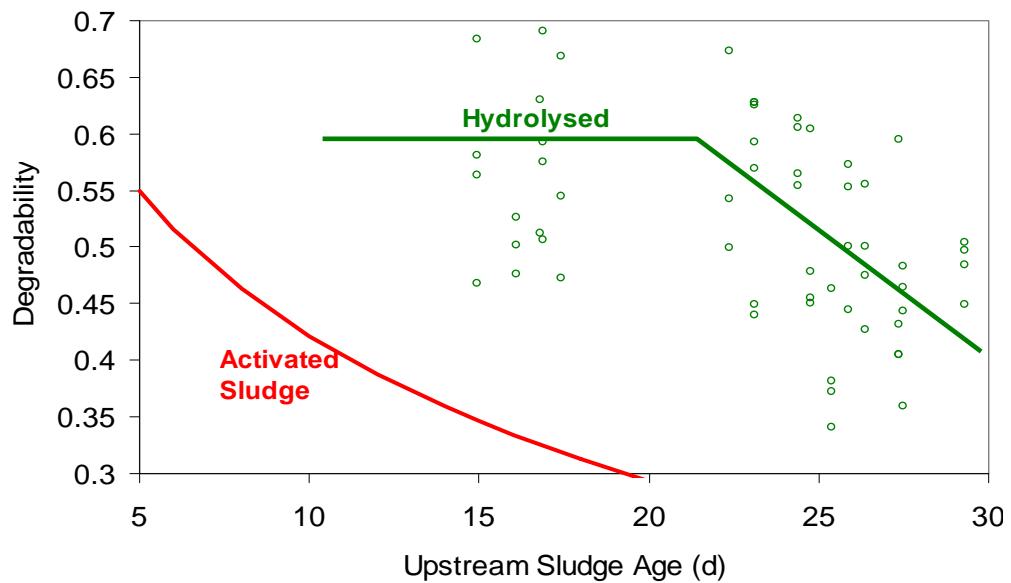


Figure 2 Thermal hydrolysis increases degradability, but depends on aerobic sludge age (from [1]).

Final dewaterability is strongly improved, easily achieving a 25% solids cake on poorly dewaterable material, and up to 40% on optimal material. There are some indications that solids capture may drop slightly.

The main negative impact on digester operation can be an increase in ammonia, which can cause ammonia inhibition ([2]. This can be managed by dilution, and acclimatisation appears to be rapid.

The other impact that has been observed on plant wide operation is an increase in soluble coloured byproducts. This can cause 30-40 mg Pt/Co in the effluent [3], with 1-2 mg/L N as dissolved organic nitrogen. The colour will decrease the efficiency of UV sterilisation. This is only a problem where UV sterilisation is applied, or where effluent nitrogen limits are very strict (and include organic nitrogen).

5.4 PROCESS DESCRIPTION

5.4.1 Basic Aspects

Pre-dewatered sludge, up to 15% solids concentration, is added to the pulper where it is held until the reactor is ready for a batch conversion. Sludge is then pumped to this reactor where it is held for a minimum of 20 minutes at 150-170°C and 5-8.5 bar. Live steam is added to achieve this temperature and pressure. Steam is vented to the feed tank for multiple effect heating. At the end of the batch, solids are allowed to flow to the flash tank where the rapid expansion (back to 3 bar) causes the cells rupture and liquefy with resultant decrease in viscosity. The final concentration is 10 - 12%, suitable for mixing in the digester. While the whole sludge stream is treated, it is primary activated sludge that is improved. Therefore the process can be more cost effective by applying thermal hydrolysis only to the secondary sludge, thus reducing the tankage and the steam required. The secondary sludge could then be mixed with unheated primary sludge to reach the temperature of 37-38°C required for mesophilic digestion. The Cambi thermal hydrolysis system is modular, with the limitation being the reactor vessel, which has a maximum size of 12 m³. One reactor can treat 4,000 to 5,000 dry t/year, with a 90 minute cycle time for each batch feed. This is equivalent to a treatment plant with a flow capacity of around 40.000 to 50.000 m³/d. The size of one train is limited to six reactors in parallel, with one pre-heat tank and one flash tank per train. Larger systems will require multiple trains.

5.4.2 Equipment

The following plant list is the preliminary design specifications for all major components in the THP.

All specifications are subject to changes as a result of the detailed engineering.

Table 2

No. off	Component	Specification
1 per stream	Pulper	Type : Pressure vessel Volume : 26 m ³ : 3 bar g: 60 - 110°C Pressure Temperature
2 per stream	Circulation pumps	Type : Eccentric screw pump Capacity : 45 m ³ /h Head : 1 bar DS : 10-14% Temperature : 50-100°C
2 per stream	Reactor feed pumps	TypeCapacity : Eccentric screw pump: 45 Head m ³ /h: 2 bar DS : 10-14%: 50-100°C Temperature
3 per stream	Reactor	Type : Pressure vessel : 12 m ³ : Volume 12 bar g: 150 - 180°C Pressure Temperature

No. off	Component	Specification
1 per stream	Flash tank	TypeVolumePre : Pressure vessel: 26 m ³ ssure : 3 bar g Temperature : 70-115 °C :
3 per stream	Digester feed pumps	TypeCapacity : Eccentric screw pump: 24 Head m ³ /h : 3 bar DS : 8 – 12 %: 90°C Temperature
1 per stream	Foul gas cooler	Type : Tube in tube exchanger Cooling : Final effluent water medium
1	Foul gas compressor skid	Type : TBA Capacity : TBA m ³ /h: 3 bar Head : 20-50°C Temperature

5.4.3 Control System

The control system is designed to ease the operation of the THP plant.

By using the system, the operators can:

Enable and disable the THP plant operation

Monitor system status

Specify operational parameters

Acknowledge and reset faults

Specify trends

5.4.4 Operation and Maintenance

The plant is designed for automatic 24 hour per day operation 7 days per week (24/7) with daytime attendance for routine operational checks, 5 days/week. In order to handle alarms and reduce downtime in case of automatic shutdown a callout organisation should be established operating on a 24/7 basis.

Life expectancy Thermal Hydrolysis Plant

The reactors are designed for 130,000 cycles of 90 minutes with 100% safety margin according to PD5500. The expected design life of a plant is from 22 – 32 years depending on the number of reactor cycles per year. This life expectancy is based on the following conditions:

The chloride concentration in the sludge does under normal operational conditions not exceed 400 mg/l.

Necessary average yearly budget for maintenance is 2% to 3% of the investment cost for the quoted plant. This covers both personnel and parts on a 50/50 split. Maintenance personnel should be available daily (8/5), and on callout during nights and weekends if required.

Preliminary recommended spare parts:

Pump groups: Two stators and one mechanical seal for each group of pumps.

Circulation pumps: According to recommendation from supplier.

Foul gas compressors: According to recommendation from supplier.

Valves:	One of each type and size of manual valve One of each type and size of automatic valve
Instruments:	One complete instrument per type
Gaskets:	Several of each size (spiral wound)

In addition to this the suppliers need to keep electrical parts, such as frequency converters, relay and switches, in stock for delivery within 3 days.

5.5 COSTS

Table 3 Operating costs for 20.000 dry ton/year Cambu plant based on

CHERTSEY STW OPERATING DATA		
Electricity	259,881	kWhs
	13	kWh/dry ton
Chemicals	£41,000	€49,200
Consumables	£37,200	€44,640
refurb fund	£7,440	€ 8,928
Total	£85,653	€102,784
Capital Cost		€4,000,000
Maintenance costs as % of capital		2.6%
Labour	£83,333	€100,000
Total	£168,986	€202,784
cost per tds	£8.45	€10.1

5.6 FULL SCALE EXPERIENCE

5.6.1 WWTP Hamar (NOR) (90,000 p.e.)

The thermal hydrolysis part of the overall treatment process consists of two pulping tanks, one reactor tank and one flash tank. The sludge is fed into the pulping tanks where it is homogenised, pre-heated and cut to a particle size of less than 3 mm in a macerator pump. It is then passed to the reactor tank for thermal hydrolysis by treatment at high pressure (around 10 bar) and temperature (160°C) for 30 minutes. The pressure and temperature are reduced in the flash tank. The average operating parameters are shown in table 2.

Table 4 Average values of Hamar operating parameters

Water consumption for steam production	2,500 m ³ /year
Live steam for the hydrolysis process	8,800 kWh/d
Recovered energy (at flash tank heat exchanger)	6,100 kWh/d
Net energy consumption for hydrolysis	2,700 kWh/d
Net energy production in digester	15,000 kWh/d
Surplus energy	12,300 kWh/d
Volume treated	2,700 dry t/year
Mass reduction	50%
COD removal	59%
Gas production	2,500 Nm ³ /d (70% methane)
Dewaterability of digested sludge	35% can be achieved, currently 28%

At this moment the energy content of the biogas is solely used for heat generation.

The thermal hydrolysis module has been operated continuously since the start at the turn of the year 1995/96.

Earlier thermal hydrolysis processes gave problems with wear on the valves; this problem has been minimised by reducing the temperature and the pressure stepwise. The flash tank was designed to shut down the hydrolysis plant during the weekends, however since the hydrolysis plant can be operated 24 hours a day, the tank is oversized. To minimise the total energy consumption, a heat exchanger transfers heat from the flash tank back to the pulping tank to assist the pre-heating. The daily operation of the entire sludge treatment, including external sludges, is today in the hands of one operator. The plant's maintenance staff contributes with 1/3 of a man-year. The steam boiler operation calls for people with a boiler certificate. The steam boiler needs to be inspected every 84 hours. An inspection includes water analysis, leakage control, and general maintenance control.

The thermal hydrolysis of sludge releases strong odours. An installed biofilter proved to be insufficient, currently the air is injected into the aeration basins of the activated sludge process (Fjærgård T. and Sander O., 2002).

5.6.2 WWTP Ringsend (Dublin, Ireland) (1.6 milion p.e.)

Sludge is pasteurised and hydrolysed thermally by holding a batch at 165°C for 24 minutes at 6 bar pressure. The combination of the high temperature during the cycle and the pressure drop at the end of the cycle breaks open cells making the sludge more readily biodegradable. The Dublin WW treatment plant (Figure 3) treats up to 11.3 m³/s of flow. The equivalent population is 1.6 million of which ½ million is industrial load.



Figure 3 View of the Dublin WW treatment plant

All the sludge at Dublin is screened through 10 mm sludge screens, pre-dewatered and then fed to the CAMBI process. In the Cambi process the pressure is raised to 6 bar whilst the temperature rises to 165°C in batches of about 7.5 m³. This condition is maintained for 24 minutes, a time established as optimum for the nature of the sludge in Dublin.

The Cambi thermal hydrolysis plant at Dublin heats the sludge under pressure, the hydrolysis converts approximately 50% of the biological and 10% of the raw particulate COD to a more digestible form.

A blended primary and activated sludge mix is pre-dewatered at concentration higher than 18% using centrifuges. The cake is then diluted with hot water (Brian Pickworth et al.). The sludge passes through two stages of pulper tanks where it is homogenised and heated up to 100°C with recovered steam from the process. The sludge is fed to one of eight batch reactor tanks where it is heated to 165°C and put under at least 6 bar pressure. The cycle time from starting to fill a reactor to when a reactor is empty is typically 90 to 110 minutes.

The hydrolysed sludge is passed to a flash tank, to a heat exchangers and then to the digesters. Steam produced in de-pressurisation from 6 bar to atmospheric pressure is directed back to the two pulpers to pre-heat the sludge.

The plant runs 24 hours a day processing 90 - 100 dry t/d. As a result of the hydrolysis process the subsequent digestion stage achieves a reduction in volatile solids of 62% and a reduction of dry solids of 50%. Thus the 100 tonnes fed to the process results in only 50 tonnes for drying and shipping off to agriculture.

The biogas production has been stable at approx 0.7 m³/kg VS destroyed and this

has correlated well back to the COD fractionation of the wastewater and site sludge production.

The digesters are fed with a hydrolysed and pasteurised sludge at 11-12% solid and operate at 15 days hydraulic retention time. The 4,250 m³ Dublin digesters (bottom fed and mechanically mixed) are currently loaded at 6 kg VS/(m³ × d). The digesters are stable with ammonia concentrations over 2,000 mg/L as the pH is between 7.6 and 8.0 units. Thermal pre-treatment inhibits foaming. The microbial community in the digester is stable because the digester is fed by a sterile sludge. Both systems are energy neutral because the heat required to treat the sludge is recovered from the engines that burn the biogas to produce electricity or the steam boilers running on biogas.

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6

PRODUCTION OF BIOPOLYMERS FROM WASTE BIOSOLIDS

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. However, in the context of this technology, biosolids represent a high volume, renewable resource rich in organic carbon that can be transformed into a usable product, namely bioplastic (Figure 1). Bioplastics, such as polyhydroxyalkanoates (PHAs), are polymers synthesised by bacteria. They can replace parts of the market of conventional plastics such as polypropylene and polyethylene since PHAs possess similar thermoplastic properties [1]. A major advantage of PHA bioplastic is that it 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.

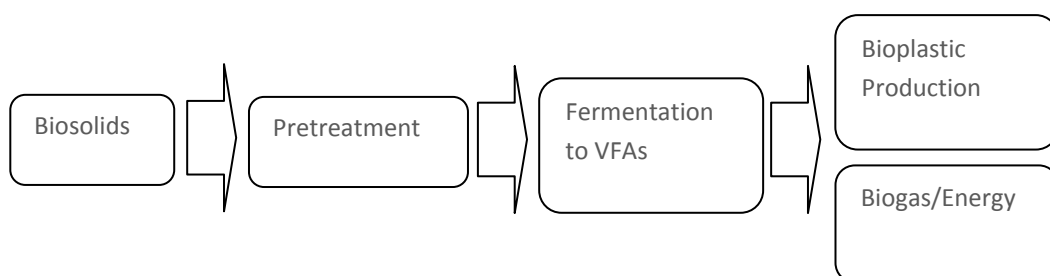


Figure 1 Strategy for utilising biosolids to produce biopolymers and energy. Volatile fatty acids (VFAs) produced during fermentation are the ideal feedstock for biopolymer production.

PHAs can be produced by open, mixed bacterial cultures utilising inexpensive and renewable carbon sources, namely waste streams, e.g., fermented pretreated biosolids. Biosolids have been identified as a potential substrate since they are abundant, regular in concentration and contain biodegradable carbon. For example,

a moderate sized wastewater treatment facility (500 000 PE) handles in the order of 50 000 tonnes of carbon rich biosolids per year (10-15 % DS).

6.1.1 Integrated process

This technology considers the utilisation of pretreated biosolids as carbon-rich resource for biopolymer production in tandem with biogas/energy generation. Pretreatment involves in this case high pressure thermal hydrolysis (HPTH) (e.g., Cambi or Biothelys processes) to solubilise suspended matter by hydrolysis at high temperatures (100-180°C) and pressure (6 bar) at a retention time of approximately 30 min; however, other pretreatment could be considered. 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. A proposed overall flow diagram for producing PHA biopolymers from thermally hydrolysed sludge is presented in Figure 2.

Performance parameters are described below with exception of the downstream processing units (Figure 2).

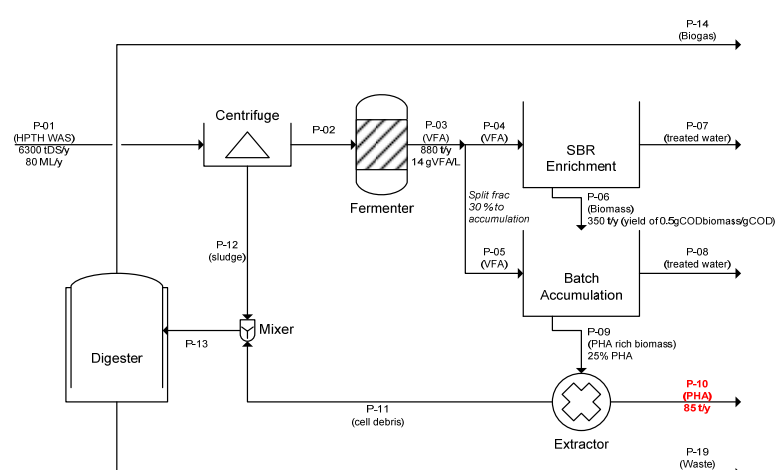


Figure 2 Proposed process flow sheet for producing PHA biopolymers from thermally hydrolysed sludge (Including flow rates of major streams). Basis: HPTH-WAS flow (6300 tDS/y) from Oxley Ck (Brisbane, Australia) CAMBI process

Permeate collection. A centrifuge (potentially 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 1) under which conditions the VFA production rates are high due to high throughput in comparison to fermenters treating untreated WAS, which would require a larger fermenter.

Table 1 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 (°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 m³ day⁻¹. Consequently, to support a 1 d retention time, a fermenter in the order of 200 m³ would be required.

The VFA yield for 1d retention time is in the order of 1 gVFA 5 gTCOD⁻¹ (or 20 gCOD_{VFA} L⁻¹). The relative portions of VFAs produced (on a COD basis) are shown below in Figure 3.

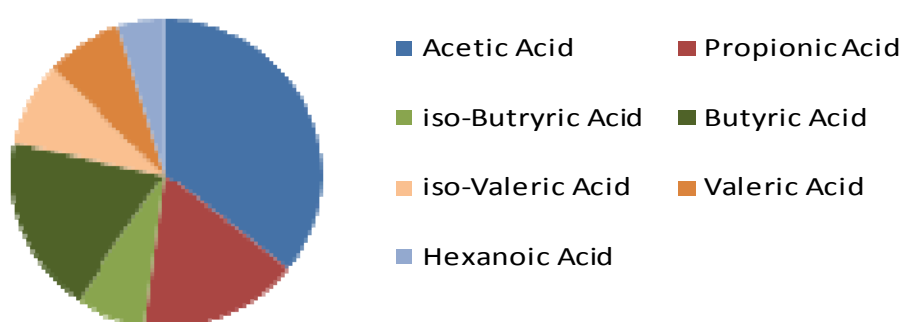


Figure 3 Spectrum of VFAs produced (avg 1.5gCOD/gVFA)

Enrichment of PHA-storing organisms. The operating conditions of the SBRs investigated in this research enriching for PHA-accumulating organisms are presented in Table 2. 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 2 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 an aerobic batch reactor for PHA accumulation operated with a retention time of 8 hours 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 [2].

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INSTRUMENTATION, CONTROL AND AUTOMATION

7.1 INTRODUCTION

When confronted with increasing loads or stricter effluent limits, plant operators/managers generally have three options. The plant can be increased in size (extra aeration tanks, post-treatment, pre-treatment...), optimization methods can be applied to select adequate operating conditions and measuring and control concepts can be used to reach the new goals with the existing infrastructure [1]; [2]. The last option can save considerable amounts of money and resources and is considered environmentally friendlier.

Even without increasing loads and/or stricter limits, automatic control is often preferred over manual control since it generally results in a better effluent quality at a lower cost. This is not only helpful to deal with changes in diurnal, weekly or seasonal loads, but it is also helpful to predict future loads.

7.2 DESCRIPTION

7.2.1 Basic aspects

Objectives for control

The implementation of ICA in wastewater treatment plants has been demonstrated to be useful to optimize process performance by adapting the process operation according to the local environmental conditions and the process requirements. Control algorithms translate the information of the sensors (inputs) into actions for the actuators (outputs). Different objectives for the wastewater treatment plant operation lead to different control actions and trade-off situations (e.g. improving effluent quality might be associated with increasing costs and increased carbon footprint). Ideally calibrated, plant specific, dynamic mathematical models are available with which the best algorithm and settings can be selected to reach the desired objective.

Objectives could be:

- Comply with legislation on effluent concentrations
- Reduce costs
- Reduce environmental impact (e.g. reduce carbon footprint)
- All possible combinations of the above defined objectives

Control loops

The control algorithms translate the information of the sensors (inputs) into actions for the actuators (outputs). In order to describe a control loop the following terms are defined:

- Disturbances: variables that change and affect the process but over which we have no direct control.
- Manipulated variables: those variables affected by the actuators and which have an effect on the process.
- Measurements: signals that we get from the sensors.

Depending on the type of physical and data flows two different control loops are considered, feedforward and feedback (see Figure 1). In feedforward control loops an action can be initiated before the disturbance causes effects on the system. The difficulty with feedforward control is that the effect of the disturbances on the system must be accurately predicted with a model. In a feedback control loop, the measured variable (S) is compared to the reference value that is selected and the error is used to calculate the actuator (A) action that will drive this error to zero. The disadvantage is that an error must already occur before action is taken (it is corrective in nature).

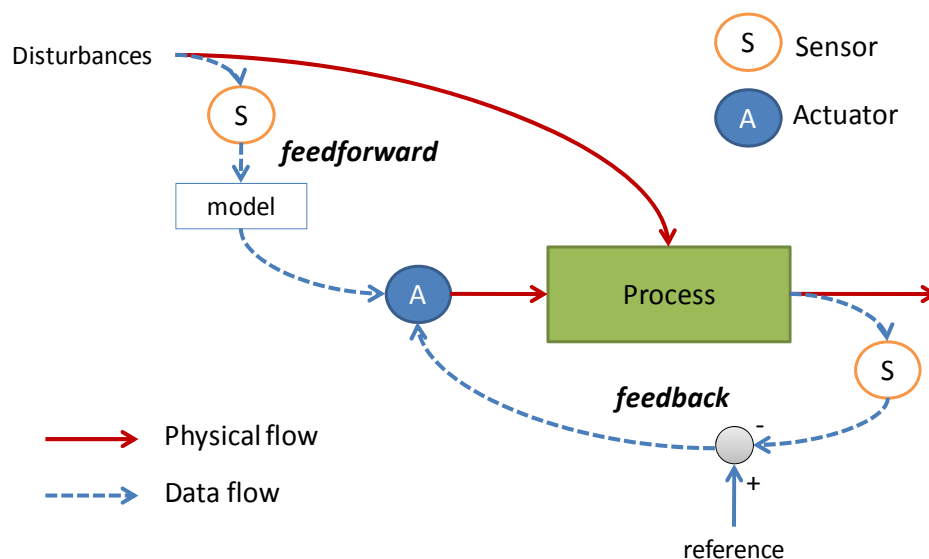


Figure 1 Feedback and feedforward control

As an example the control of aeration is presented. In this case, aeration is controlled with the objective to reach good effluent quality (especially regarding nitrogen concentrations) and save energy. Aeration is

used to regulate the nitrification and denitrification processes. For this case, different possibilities are shown in Figure 2. The first possibility is to maintain the dissolved oxygen concentration (O_2) at a setpoint value (defined from experience or optimization studies) using a feedback PI controller. The second possibility is to add a PI controller to maintain the ammonium concentration at a setpoint value. Therefore, ammonium is measured and a master controller determines the O_2 setpoint of the slave PI O_2 control.

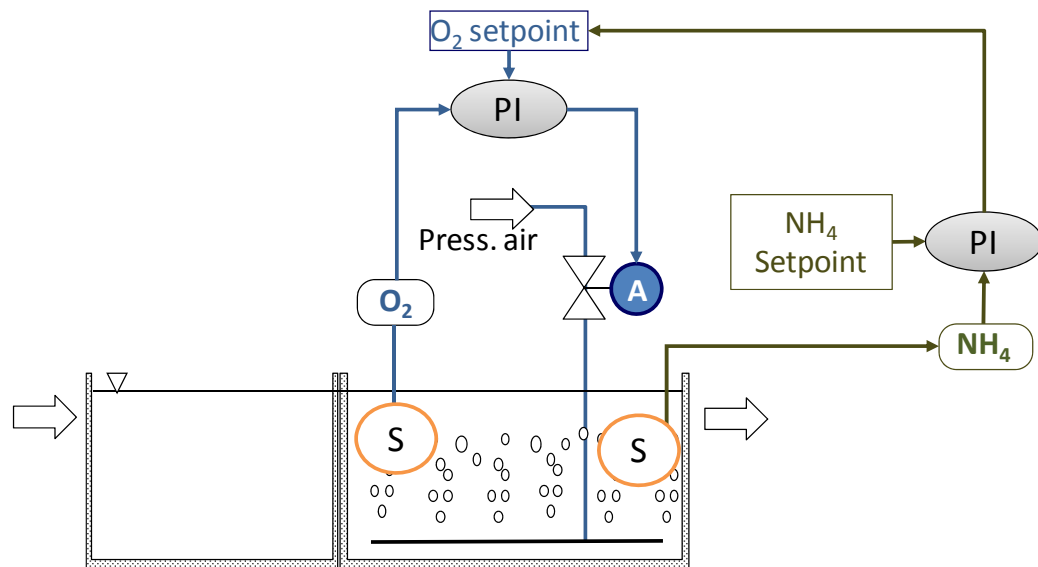


Figure 2 Aeration control (NH_4^+ feedback control)

Many control algorithms have been proposed in the literature ranging from simple classical control (On-Off, P, PI, PID), to model-based control (such as model predictive control), adaptive control,, rule-based control, neural network and fuzzy control.

7.2.2 Equipment

Basically, the devices used for control implementation are: sensors, actuators and controller equipment.

Sensors

The performance and reliability of many online sensors (e.g. nutrient sensors, flow and level meters) have improved remarkably during the last decade and can be used for process monitoring, but they can also be used in many different control strategies [2]. There are numerous sensor systems available in the industry, and different possible classifications can be done [3]:

- Classification based on the functional application of the sensors:
 - use in automatic control systems,
 - use for monitoring purposes, i.e. providing information about the state of the plant.
- Classification based on the configuration of the monitoring systems (see Figure 3):
 - in-situ sensors: often simple, and low maintenance sensors that are used in trend monitoring and, due to their often short

response time, in automatic control systems and

- ex-situ analyzers: often more complex maintenance-intensive analyzers that are typically found in plant effluent monitoring (because of the normally high accuracy).
- Classification based on the capacity of the sensor to be used in different locations of the wastewater treatment plant
 - influent,
 - activated sludge reactor...
- Classification according to different measuring principles:
 - colorimetric
 - potentiometric
 - ion sensitive
 - optic

More information can be found in Vanrolleghem and Lee [3].

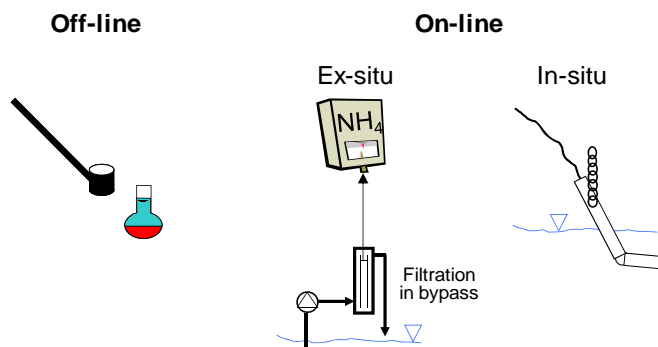


Figure 3 Definition of measuring systems based on sampling and installation

Table 1 presents a summary of different sensor technologies available, classified according to functional application, location and measuring principles.

Table 1 Objectives of control versus measuring principles (GS: Gas Sensitive, IC: Ion Chromatography, UV/VIS: Ultraviolet-visible optical measurement, TSS: Total Suspended Solids, Inf: Influent of WWTP, AS: Activated Sludge reactor, Eff: Effluent of WWTP)

		Ex-situ							In-situ				
Objective		Ammonia Colorimetric. IC. GS Nitrate.nitrite Colorimetric. IC. UV Ortho-Phosphate		P-total Thermal chemical TOC. DOC. COD. BOD		Dissolved oxygen	Turbidity. TSS	pH. redox. conductivity	Ammonia Ion sensitive electrode Nitrate. nitrite UV. Ion sensitive Organic compounds UV/VIS		Sludge level		
Inf	Load monitoring												
	Equalization of load				X		X	X	X		X		
AS	Aeration control	X	X			X			X	X			
	RAS. internal recycle		X							X			
	WAS control/monitoring						X				X		
	P precipitation			X									
	Dosage of carbon source		X							X	X		
Eff	Monitoring	X	X	X	X	X	X	X	X	X	X		
	Control of P precipitation								X	X			

The demands on the measuring equipment are decreasing with ongoing treatment steps. Whereas only few sensors are robust enough to deal with the harsh conditions and the difficult water matrix in the WWTP influent, most available sensors can be used to monitor the effluent quality. The final choice should depend on the objective of the measurement. If the goal is to monitor whether the plant complies with the effluent limits the most accurate sensor should be used. The best choice is then probably an ex-situ analyzer with auto-calibration.

Actuators

In a wastewater treatment plant the actuators regulating the process are grouped in different types: the hydraulic-related variables (internal recirculation, external recirculation, sludge wastage, reject water recycle, by-passing pumps...), aeration and chemical addition variables. Figure 4 presents a scheme of a typical wastewater treatment plant consisting of a primary sedimentation tank, aeration tank and secondary clarifier with its actuators and the main effects they have on the process when manipulating them. In Figure 4 it can be seen that there is a limited number of actuators and that a single actuator might have an effect on different processes and relevant variables (nitrification, denitrification, phosphorus removal efficiencies, sludge and hydraulic retention times and costs). This is the reason why one should study the control of a plant from a plant-wide perspective.

The range of manipulation of these variables is limited by physical, process or economic constraints. Some of the key manipulated variables and their limits are described below.

Manipulation of wastage flow rate: Wastage flow rate is used to control the Sludge Retention Time (SRT) of the system (directly related to the MLSS concentration in the reactors). The minimum and maximum boundaries for selecting the SRT are:

- Minimum boundary: The minimum SRT should be high enough to allow nitrifier organisms to grow in the system with a certain safety against washout. In winter the solids concentration in the reactors can be increased to make sure that the nitrifiers are not washed out.
- Maximum boundary: The maximum MLSS concentration value is selected according to the maximum capacity of the secondary clarifier. One has to take into account that at a higher MLSS concentration and therefore higher sludge age a) the sludge production decreases, b) the oxygen demand increases due to higher endogenous respiration in the activated sludge tank and c) the biogas production in the digester is reduced.

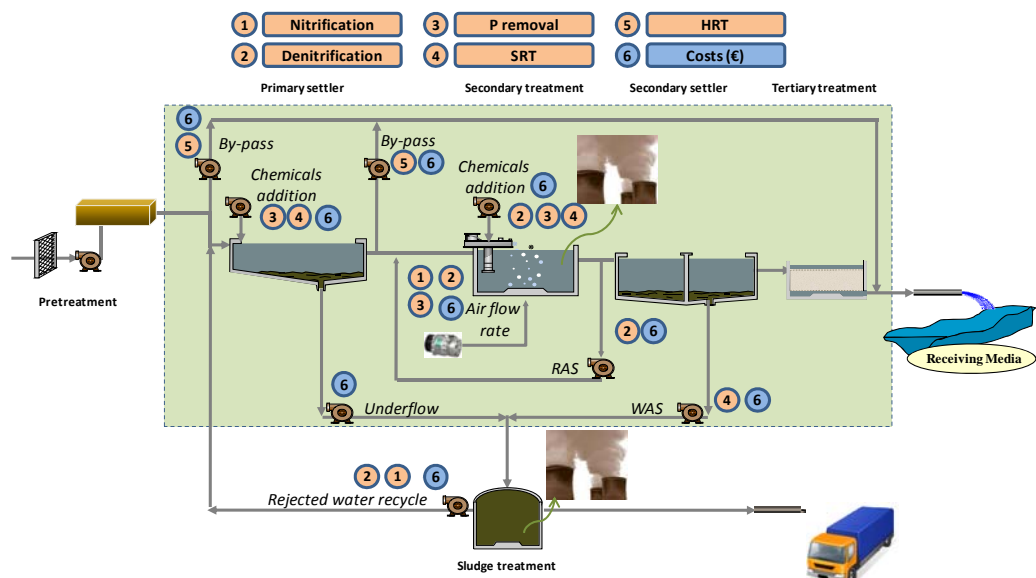


Figure4 Schematic outline of control options and main effects (numbers in circles) in a wastewater treatment plant. In green the water line.

Manipulation of internal recirculation of nitrates: In predenitrification activated sludge systems the internal recirculation is used to bring the nitrates generated in the aerobic reactors (nitrification) to the anoxic tanks where the denitrification occurs. The minimum and maximum boundaries are determined by the following:

- Minimum boundary: A minimum flow rate is required to transfer the required nitrate to the anoxic reactors to achieve good nitrate concentrations to denitrify (normally values between 1 and 2 mg $\text{NO}_3\text{-N/L}$ are pursued at the end of the anoxic zone).
- Maximum boundary: This is determined by the maximum capacity of the pump. Moreover, one has to take into account that a too high internal recirculation rate might bring too much oxygen into the anoxic reactor that will reduce the denitrification rate.

It is important to state that the internal recirculation is not sensitive if organic

matter limits the denitrification [4]

Manipulation of aeration: The airflow rate supplied to the reactors is the most studied manipulated variable. As presented in Figure 4 it influences all biological processes and it causes a significant part of the operation costs. The minimum boundary is selected according to the oxygen requirements of the process or mixing power to maintain the sludge in suspension and the maximum boundary is related to the costs.

Chemicals addition: The most common chemical compounds added in the WWTPs are 1) the external carbon sources for systems with limiting biodegradable substrate with the aim of improving denitrification and biological phosphorus removal and 2) the iron/alum salts for phosphate precipitation. The dosing location is crucial to maximize the benefits of adding the chemical. In the case of external carbon sources the addition is depending to the nitrate concentration at the end of the anoxic reactor and is conducted at the beginning of the anoxic zone. Iron/alum salts are added proportionally to the concentration of phosphorus in the reactors and/or inlet P-load. For the salts three possibilities are available: pre/post and simultaneous precipitation. For chemicals addition the maximum boundary for chemicals addition is imposed by the costs and the increase in the solids concentration of the reactor that could overload the secondary settler. The minimum boundary depends on the desired effluent quality.

Manipulation of digester reject water recirculation: Reject water coming from the digesters (that normally passes through a buffer tank) and recycled at the beginning of the WWTP can represent up to 20-25% of the total nitrogen incoming load [5]. Therefore, a common practice is to manipulate the flow coming out from the buffer tank to make sure that this water with high nitrogen concentration does not overload the system.

Other equipment

Sensors are connected to a controller unit which sends the measurement signal to a controller (PLC). When control is applied the PLC is responsible for the lower level calculations which lead to the actions. Generally wastewater treatment plants are equipped with SCADA systems (*Supervisory Control And Data Acquisition*) that allow remote monitoring and controlling of the process. Typically, the SCADA systems take care of higher level decisions for monitoring and control (e.g. supervisory control).

7.2.3 Maintenance - operational stability – safety requirements

Maintenance. As a rule of thumb sensors should be cleaned and checked on a weekly basis. Some online ammonia and phosphate measurement still require reagents. However, reagent free and reliable dissolved oxygen, suspended solids, ammonia and nitrate sensors are available. Operational stability of this new and cheaper generation of nitrogen sensors is currently being investigated.

Controller tuning. The parameters of the controllers have to be adjusted to obtain good performance. In practice, standard algorithms with standard settings are used. Ideally, dynamic mathematical models can be used to better tune the controllers.

Safety. Fall back strategies in case of sensor failure should be included in the control algorithms and ideally sensor failure detection systems should be installed to allow safe operation.

7.3 COSTS

The benefits of ICA can be:

- Operation cost reductions
- Investment substitution or delay
- Improved effluent quality
- Increased stability of operation

ICA also comes with an investment and operational cost:

Investment costs:

- Sensors, actuators and controllers
 - Oxygen sensor: $\pm \text{€ } 1500$
 - NH_4 sensor (ion selective): $\pm \text{€ } 4000$
 - NH_4 sensor (colorimetric): $\pm \text{€ } 12000$
 - NO_3 sensor (254 nm): $\pm \text{€ } 12000$
- Instrument and network cabling (cables cost a lot of money if not laid during the construction phase of the plant, modern controllers have the ability to transfer data wireless)
- Training
- Controller development costs
- Software

Operational costs:

- Sensor recalibrations and maintenance
- Sensor chemicals, filters, etc,

Usually the reduced energy and chemicals demand outweighs the cost of ICA. The payback of intelligent control is determined by the plant size. A dynamic model of the WWTP allows correct calculation of the payback times [6].

7.4 FULL SCALE EXPERIENCE

Online control using sensors started in the 1970s when the sensors reached a level of precision suitable for control. The main focus at the beginning was on studying control for aeration (e.g. [1]) and since then control for other elements of the plant have been developed. In recent years ICA of WWTP's has reached maturity, what can be illustrated by describing the experiences of Aquafin NV⁴.

All activated sludge WWTP's run by Aquafin (more than 220) are equipped with one or more oxygen sensors (to control aeration), a turbidity sensor in the effluent and an MLSS sensor in the aeration basin (to control solids concentrations). Some WWTP's have sludge blanket sensors that are used to reduce suspended solids washout. A large number of gravity thickeners are equipped with MLSS sensors to achieve the highest possible thickening without spilling suspended solids in the overflow.

Nitrogen sensors were introduced in the year 2000. At that time nitrogen sensors were quite expensive and the only driver for installing nitrogen sensors was the reduction of operational costs. It was calculated that the payback time was less than 3 years for plant sizes larger than 50000 PE. By the end of 2005 Aquafin NV was confronted with stricter effluent standards. Also a new control algorithm was developed that allowed online control of the length of the aerated phase with only a nitrate sensor (without ammonia sensor). Consequently also the smaller plants (lower than 50000 PE) were equipped with on line aeration control. By the end of 2010 the length of the aerated phase will be controlled by one or more nitrogen sensors (NO_3^- , NH_4^+) in 90% of them. The evolution of the number of installed sensors up to 2009 is illustrated in Figure 5 and Figure 6.

⁴ Aquafin designs, finances, builds, optimizes and operates all supramunicipal infrastructure needed to treat domestic wastewater in Flanders. At the end of 2008, Aquafin was responsible for 228 wastewater treatment plants. Aquafin manages 4,427 km of sewer pipes. 1,026 regional pumping stations and storage basins.

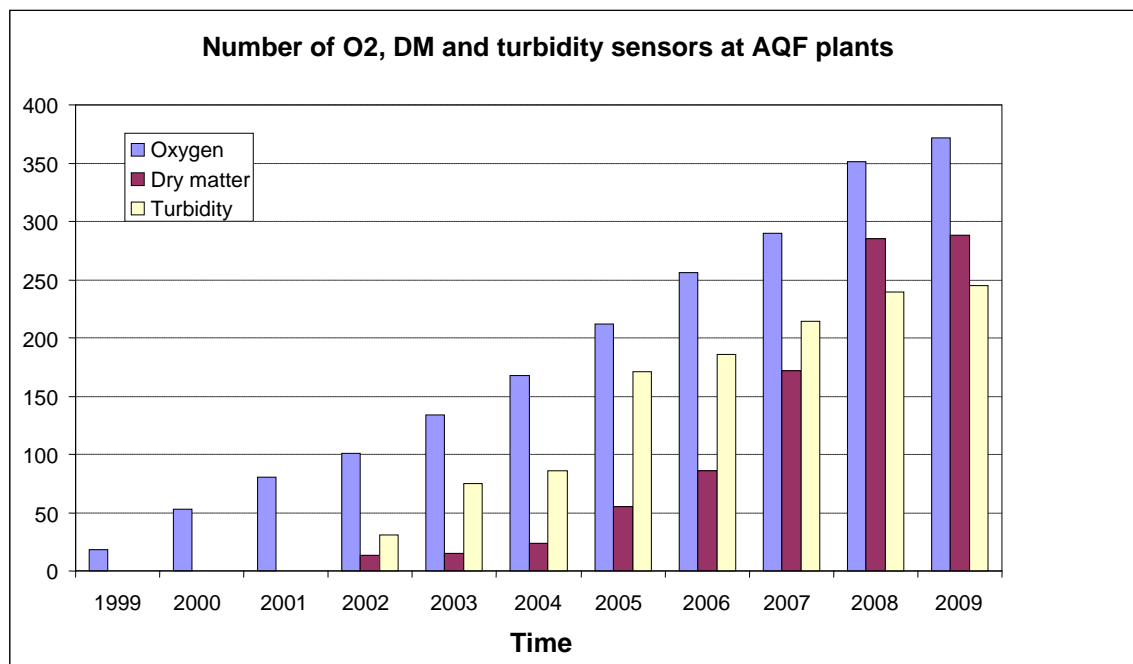


Figure 5 Number of oxygen, Dry matter and turbidity sensors at Aquafin plants

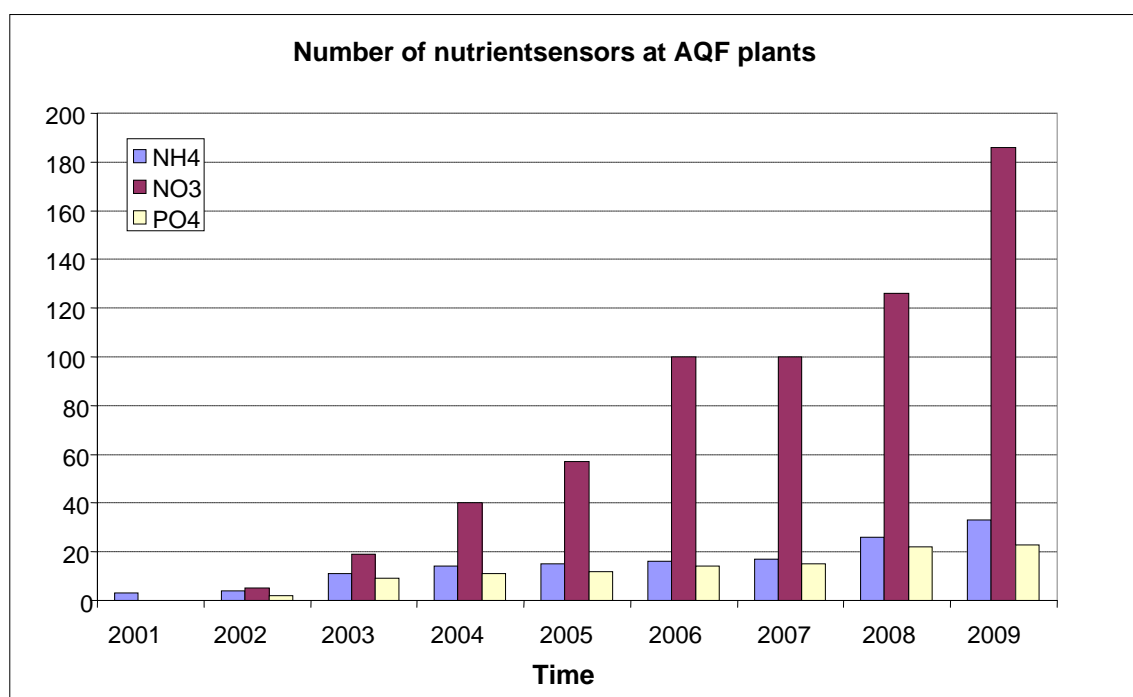


Figure 6 Evolution of the number of nutrient sensors at Aquafin plants.

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8

ZEOLITE ADDITION FOR IMPROVEMENT OF WWTP PERFORMANCE

8.1 INTRODUCTION

In plants with insufficient capacity to deal with seasonal loads, it is difficult to achieve consistent nitrification. The necessary sludge age and mixed liquor suspended solids cannot be maintained within limits that allow a good process performance and don't exceed the safe solids loading to the final clarifier. Zeolites have been used to achieve improved wastewater treatment plant performance. For example, seasonally loaded wastewater treatment plants can benefit from zeolite addition for improvement of the removal of nutrients, suspended solids and micropollutants from the water. Main benefit of the process is often the increase of the sludge age due to better sludge settling and as a result – improved nitrification even at a low temperature of 8-10 degrees C.

Zeolites have some capacity for adsorbing ammonia and their filtering abilities offer a versatile and environmentally friendly option to capture contaminants found in water systems.

It has a natural negative charge which gives it the capacity to adsorb cations and some organic contaminants and undesirable odours. The density and the characteristic of zeolite to be incorporated into the sludge allows further to significantly improve the sludge settleability.

With the contribution of the NEPTUNE project, full scale trials were conducted in the period 2007 – 2009. The experiments consisted of addition of polymer-modified zeolite (SEDIMENTIN MW) into the biological step of seasonally loaded wastewater treatment plants in Bulgaria. SEDIMENTIN MW consists of mixture of heat-activated zeolite montmorillonite. The surface of the mineral crystals is treated with a polyelectrolyte. The special effect of SEDIMENTIN MW is that it causes rapid settling of sludge in the sedimentation tank: the supernatant after sludge sedimentation is of a very good quality while bulking of sludge is prevented.

Therefore polymer modified zeolites (e.g. SEDIMENTIN MW) have the additional benefit of rapid sludge settling and preventing bulking of the sludge.

The history of zeolites began some 250 years ago by a discovery made by the Swedish mineralogist Crönsted, who found a mineral exhibiting intumescence when heated in a flame. While some forty different zeolites have been discovered in nature, more than 130 zeolites have been synthesized. Zeolite synthesis and application began in mid 30s-40s with the pioneering work of Barrer in adsorption and synthesis.

8.2 SCHEMATIC OUTLINE

In secondary wastewater treatment plants, zeolites can either be dosed at the outlet of the activated sludge tank before secondary settling (Stream I) or at the inlet of the activated sludge tank (Stream II).

The contact time associated with either location is different, resulting in different treatment outcomes.

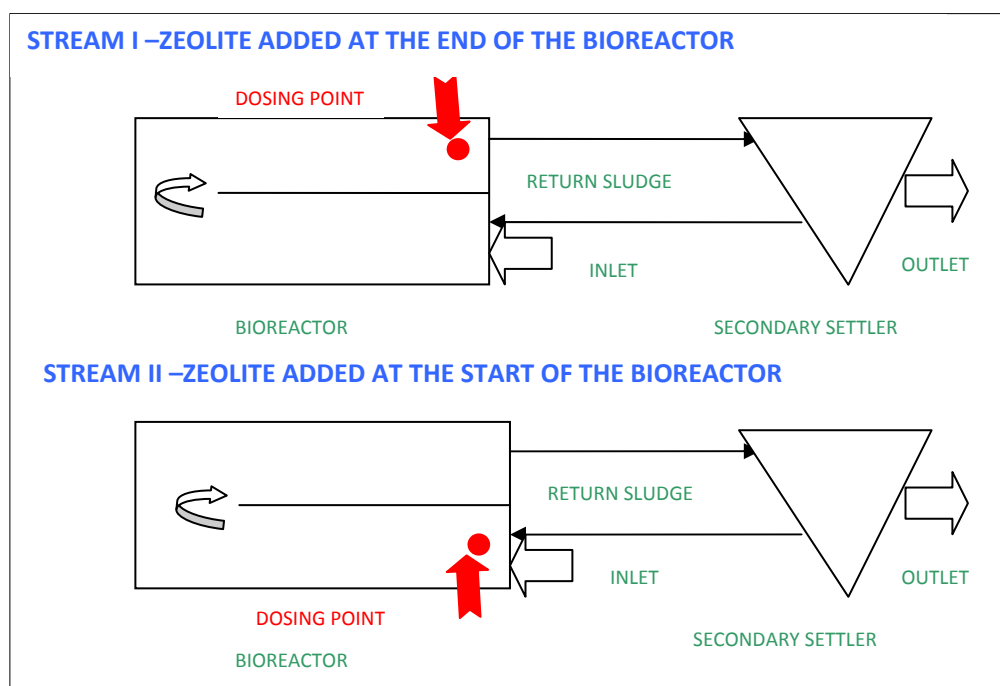


Figure 1 Flow Diagram of Secondary Biological Treatment In Wastewater Treatment Plants and Zeolite Dosing Points

8.3 WATER QUALITY

The tables and figures below summarise the effluent quality and treatment efficiency achieved in three years of experiments and compare them with the effluent quality when zeolite is not dosed.

Table 1 Average effluent quality at the Zlatni pgsyci WWTP in 2008 without and with addition of zeolite. Results are derived from 24-h composite samples.

Parameters	Effluent quality. mg/L			
	Inflow	Stream 1	Stream 2	Stream 3
BOD5	186.3	95.1	41.8	40.6
COD	479.2	306.4	176.4	170.0
N-NH4	28.3	27.5	20.5	20.7
SS	220.7	110.0	87.5	78.2
TP	6.7	6.1	4.8	5.1
TN	42.0	38.9	33.0	29.4

Stream 1: Reference stream. No zeolite dosed in the activated sludge.

Stream 2: 5.0% concentration of zeolite in the activated sludge (7 mg zeolite /L wastewater)

Stream 3: 7.5% concentration of zeolite in the activated sludge (10.3 mg zeolite/ L wastewater)

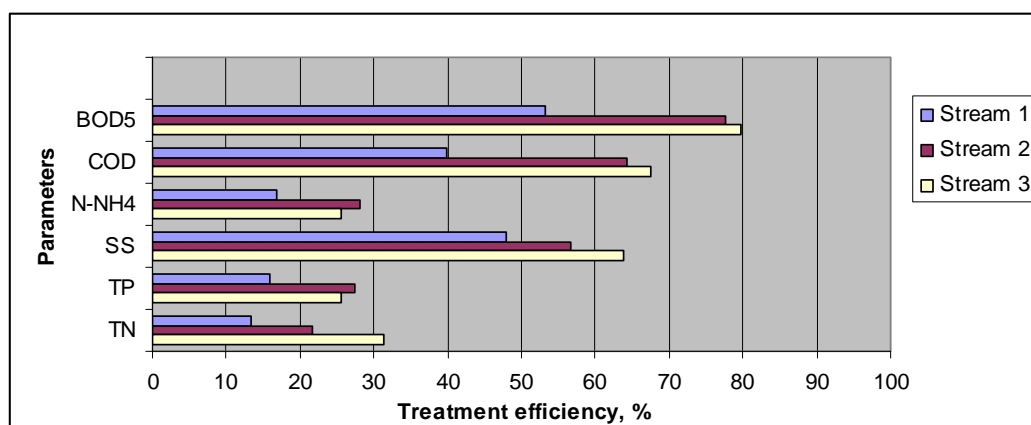


Figure 2 Treatment efficiency without and with addition of zeolite, %

Table2 Comparison of the treatment efficiency and increase of treatment efficiency achieved in the full scale experiments compared to a reference plant. Results are derived from 24-h composite samples.

		2007	2008	2009
Year		(summer)	(summer)	(winter)
Suspended solids	Dose. mg zeolite /L wastewater	16.7	7.0	10.3
	Treatment efficiency. %	64	56.8	63.7
	Increase of treatment efficiency. %	5% or less; sludge bulking	18.7	33
Ammonium nitrogen	Treatment efficiency. %	70	28.2	25.5
	Increase of treatment efficiency. %	>100	66.6	50.9
BOD5	Treatment efficiency. %	92	77.7	79.7
	Increase of treatment efficiency. %	<50	46.2	49.8

The effect of SEDIMENTIN MW on removal of micropollutants varied widely. While some micropollutants, such as antioxidants and fragrances, showed trends of reduction when zeolite was dosed, the results were not consistent and therefore the effect of SEDIMENTIN MW on micropollutants is not conclusive.

8.4 PROCESS DESCRIPTION

8.4.1 Basic aspects

The properties, and hence the application of zeolites, are mainly dependent on their structure. Some of the applications of zeolites are: adsorption; catalysis; ion-exchange and in more recent years - pollution control; remediation of mines through absorption and retention of heavy metals; fertilisers for crop yield improvements; for decrease of ammonia levels in aquaculture ponds and tanks; vermiculture and others.

Zeolites are highly selective scavengers of a variety of metal cations that can be removed from liquid effluents through the process of ion exchange. Natural zeolites are excellent ion exchangers for the removal and recovery of heavy metal cations from drinking and wastewaters. The structurally modified zeolites adsorb pollutants and floating bacteria to the mineral surface, which results in high speed of interaction and waste decomposition. The very high internal specific surface area is a substrate for bacteria and favours bacteria multiplication. This area varies with the

type of zeolite and can be as high as 500 m² per gram for the clinoptilolite.

When developing applications for zeolites, it is important to keep in mind that not all of these minerals are the same. It is critical to understand how zeolites differ so that only the appropriate types and source materials are selected for each application.

Zeolites have varying physical and chemical properties - crystal structure and chemical composition account for the primary differences. Some other properties to consider are particle density, cation selectivity, molecular pore size and strength. For example, clinoptilolite, the most common natural zeolite, has 16% more void volume and pores as much as 0.2 nm larger than analcime, another common zeolite.

8.4.2 Equipment

Automatic tenzometric dosing system was used to dose zeolite to the bioreactors. Figure 3 below shows the key elements of the system:

- a. Storage container for zeolite.
- b. Water inlet slots - allow for quick suspension of the zeolite before it is dosed in the bioreactor. The water entering through the slots provides for mixing with the wastewater to prevent formation of lumps. This part has to remain submerged below the water level.
- c. Suspension outlet slots - distribute evenly the suspended zeolite to the wastewater in the bioreactor.

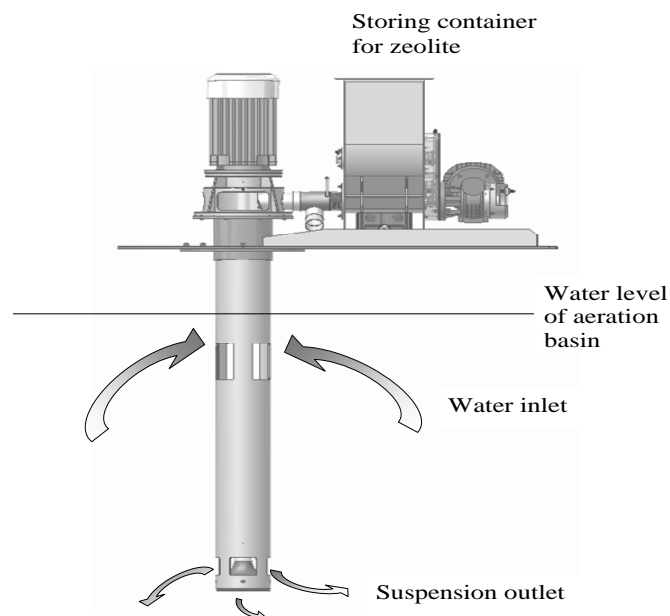


Figure 3 Zeolite dosing by automatic tenzometric dosing systems

8.4.3 Monitoring and control

Where SCADA is available, the dosing system should be connected to it for real time monitoring of the dosing parameters (influent flow, dose rate etc.) The system can be programmed to trigger dosing failure signal for prompt operator's response.

8.4.4 Maintenance - operational stability – safety requirements

The full scale experiments confirmed that blockages may occur in the dosing chute of the tensometric dosing system if the zeolite comes in contact with moist. However, the blockages can be easily cleaned by flushing with water. Daily inspection checking for blockages is a good practice. Apart from that, the process is simple and robust and no other operational problems are observed. Due to the nature of zeolites, the process poses no major hazard risks.

Care should be taken when loading the zeolite into the dosing system. Process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits should be used. Personal protection (safety glasses, lab coat, dust respirator, gloves) are to be used when handling the product. Reference to the MSDS (Material Safety Data Sheet) from the supplier should always be made for detailed information on safety, handling and first aid.

8.5 COSTS

The trial works conducted under NEPTUNE has demonstrated the potential of this technology to increase the capacity and performance of existing plants with minimal capital expenditures.

Additional cost of €0.021 / m³ was incurred for dosing 10.3 mg zeolite/ L wastewater. This was for an average daily inflow of 9 000 m³/d. The costs increased up to €0.025 / m³ with a reduction of the plant size to 630 m³/day. No additional personnel cost is expected once the system is set and operational, assuming that the system is monitored and maintained by the regular plant operators.

An example for costs associated with zeolite addition is presented in Table 3.

Table 3 Capital and operational costs for zeolite dosing system for 9'000 m³/day WWTP

Cost elements	Unit	Number of units	Unit price. €
Tensometric dosing unit	#	3	5000
Personnel	Hours/ week	3.0	Varies
Energy consumption	kW	0.2	Varies
Zeolite	€/ m3	0.021	-

In comparison with the alternative of construction of new infrastructure, the costs for zeolite addition are significantly lower. Still, detailed economic cost-benefit analyses needs to be done for each specific application to evaluate the total impact of zeolite addition on the overall wastewater treatment process, especially if the excess sludge cannot be used in agriculture but has to be incinerated.

8.6 FULL SCALE EXPERIENCE

Full scale experiments under the NEPTUNE project were conducted in 2007, 2008 and 2009. Major part of the experimental work was carried out at Golden Sands WWTP, Bulgaria. Figure 4 shows the automatic tenzometric dosing system installed in one of the bioreactors at the plant.



Figure 4 Zeolite dosing by automatic tenzometric dosing system at Golden Sands WWTP

Earlier work of zeolite addition has been carried out in Hungary in the late 1980s. Full scale trial programmes has been developed and applied in Queensland, New South Wales and Victoria in Australia in the 1990s.

8.7 KNOWLEDGE GAPS

Being inexpensive and an environmentally friendly technology, the limits of application of zeolite addition should be fully explored. Further investigation of the applicability of zeolite to wastewaters of various nature and quality will give more profound understanding of the extent of application of this technology.

Study of the effect of zeolites on industrial wastewaters with high organic concentration will allow expanding the knowledge and possibly the boundaries of

zeolite application.

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9

COMBINED NITRITATION/ANAMMOX IN A SEQUENCING BATCH REACTOR

9.1 INTRODUCTION

Partial nitritation and anoxic ammonium oxidation (anammox) in a single sequencing batch reactor (SBR) is suitable for the removal of ammonium from wastewaters with a low biological oxygen demand (BOD) and suspended solids concentration. The successful start-up and operation of several full scale plants has confirmed it as a simple and robust treatment for digester liquid from municipal wastewater treatment plants (WWTP). Compared to conventional nitrification and heterotrophic denitrification, this process requires no external carbon source, 60% less electrical energy for the aeration, produces less excess sludge and greenhouse gas. The required reactor equipment is comparable to the conventional solutions in terms of complexity. The capability of bacteria to metabolize ammonia as electron donor with nitrite as electron acceptor was discovered in the early 1990s. Oxygen is required to partially oxidize ammonia to nitrite, but the anammox biomass itself is very sensitive to molecular oxygen. Initially, much of the research on technical applications focussed on two stage processes segregating the two biochemical steps. In spite of the progress and the high rates obtained by several groups, process reliability and the coordination of the two steps resulted in a major drawback regularly causing problems during scale-up.

In 2006, an Austrian group around Bernhard Wett was first to publish on the scaling up and operation of an intermittently aerated SBR, where aerobic ammonia-oxidizing bacteria and anammox bacteria were harboured in the same compartment. They proposed the use of pH as signal for control of nitrite formation and depletion (DEMON[®] process). By using an ion selective ammonia sensor for this purpose and controlling the aeration to keep the soluble oxygen concentration $<1 \text{ mgO}_2 \text{ L}^{-1}$, it was shown that mass transfer resistance in sludge flocs protects the anammox biomass from toxic oxygen. Letting the oxidative and the anaerobic reaction take place simultaneously in the same reactor allows simplifying the reactor operation while achieving very good performance ($>500 \text{ gN}_{\text{removed}} \text{ m}^{-3} \text{ reactor d}^{-1}$).

Thanks to the contribution of Neptune during planning and start-up, five full scale

reactors (reactor volume from 150 to 1400 m³ each) are operating since August 2007, confirming the robustness of the process. While the pH control is patented as DEMON[®] process, to our knowledge the process with online ammonia electrode is not patent protected: so far no patent claim was forwarded to the plants operating; our experience has been presented at international conferences [1].

9.2 SCHEMATIC OUTLINE

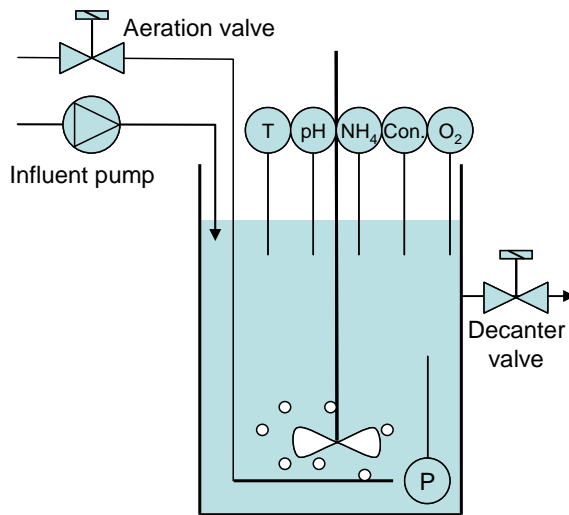


Figure 1 Schematic layout of the reactor with its principal control units: aeration device, influent pump, effluent valve and sensors for temperature (T), pH, ammonia (NH₄), conductivity (Con.), soluble oxygen (O₂) and fill level (P; pressure gauge).

A typical batch cycle is composed of the following phases: filling, aeration, stirring, sludge settling and decantation (Figure 2). During the start-up procedure and in case of little anammox activity the reactor is operated with many short aeration and stirring phases within one cycle instead of only one, in order to avoid nitrite accumulation. For stable operation the following key parameters must be controlled:

- keep NO₂⁻ below 10 mgN L⁻¹ to avoid toxic effects and to limit the growth of nitrite oxidizers
- keep O₂ below 1 mgO₂ L⁻¹ to avoid inhibiting the anammox bacteria and to limit growth of nitrite oxidizers
- avoid ammonia toxicity by keeping free ammonia <10 mgNH₃-N L⁻¹; at regular pH (7 to 7.5) and 25°C this corresponds to <200 mg NH₄⁺-N L⁻¹
- keep the temperature in the range of 20 to 40°C: since the reaction is exothermic and the supernatant mostly originates from mesophilic digestion, only isolation is required (i.e. no heating and cooling systems are required)
- pH control is normally not required due to sufficient buffering of digester supernatant

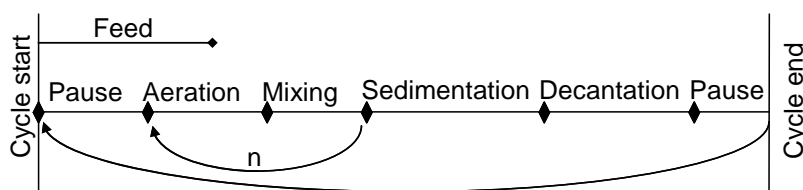


Figure 2 Phases composing an SBR cycle. *n*: repetition of aeration and stirring required during start-up.

9.3 WATER QUALITY

Ammonia content of municipal digester supernatant is normally in the range of 600 to 800 $\text{mgNH}_4^+-\text{N L}^{-1}$. By exchanging 20 to 25% of the active volume per batch, the ammonia concentration in the reactor is always $\leq 200 \text{ mgNH}_4^+-\text{N L}^{-1}$, therefore safely avoiding NH_3 toxicity. Batch termination is normally triggered at an ammonium concentration around 10 $\text{mgNH}_4^+-\text{N L}^{-1}$, i.e. for process stability complete depletion is avoided to keep some substrate for O_2 depletion during pauses intercalated between cycles.

COD has been reported to inhibit anammox, but the content present in digester supernatant (500 to 1000 mgCOD L^{-1}) is quite refractory and does not cause inhibition. Nevertheless, two events of slight activity inhibition observed during full scale operation, indicate that toxicity of specific compounds (e.g. originating from industrial co-substrate added to the digester) may still require more attention.

Table 1 Composition of the digester supernatant at the WWTP Zurich before and after single-SBR treatment. Values without standard deviation are derived from grab samples

Measurement	Unit	Before treatment	After treatment
Temperature	$^{\circ}\text{C}$	26.8 ± 1	$30 \pm 3^*$
Conductivity	$\text{mS}\cdot\text{cm}^{-1}$	5.5 ± 0.1	2.4 ± 0.2
pH		7.8 ± 0.1	7.1 ± 0.2
Ammonium	$\text{mgNH}_4\text{-N}\cdot\text{L}^{-1}$	650 ± 50	30 ± 10
Nitrite	$\text{mgNO}_2\text{-N}\cdot\text{L}^{-1}$	< 0.2	< 0.2
Nitrate	$\text{mgNO}_3\text{-N}\cdot\text{L}^{-1}$	< 0.2	5 ± 5
COD soluble	$\text{mgO}_2\cdot\text{L}^{-1}$	300 ± 50	190 ± 50
COD total	$\text{mgO}_2\cdot\text{L}^{-1}$	630 ± 50	400 ± 100
Total suspended solids	$\text{mg}\cdot\text{L}^{-1}$	250 ± 50	150 ± 100
DOC	$\text{mg}\cdot\text{L}^{-1}$	80	not measured

9.4 PROCESS DESCRIPTION

9.4.1 Basic aspects

Figure 3 shows that the anammox based process results in a smaller aeration requirement and avoids the need to dose a carbon substrate as heterotrophic electron donor. Nitrogen removal rates of up to $500 \text{ gN m}^{-3}\text{d}^{-1}$ with a degradation performance of over 90% have been reached; pilot results indicate that significantly

higher rates are feasible, but from a practical perspective this is of minor importance compared to process robustness, simplicity of operation and total costs. The process is controlled by the online ammonia signal (substitutable by the conductivity measurement combined with regular offline nitrite monitoring). Full scale runs confirm that special attention is required during start-up to assure reliable sedimentation of the sludge, while sludge with good settling capability develops during regular operation. Although the observed N_2O emissions were slightly higher than in conventional nitrogen removal, the overall greenhouse gas emissions were lower, mainly due to the energy saving (i.e. compared to conventional nitrification and denitrification; details are given in Joss et al., 2009).

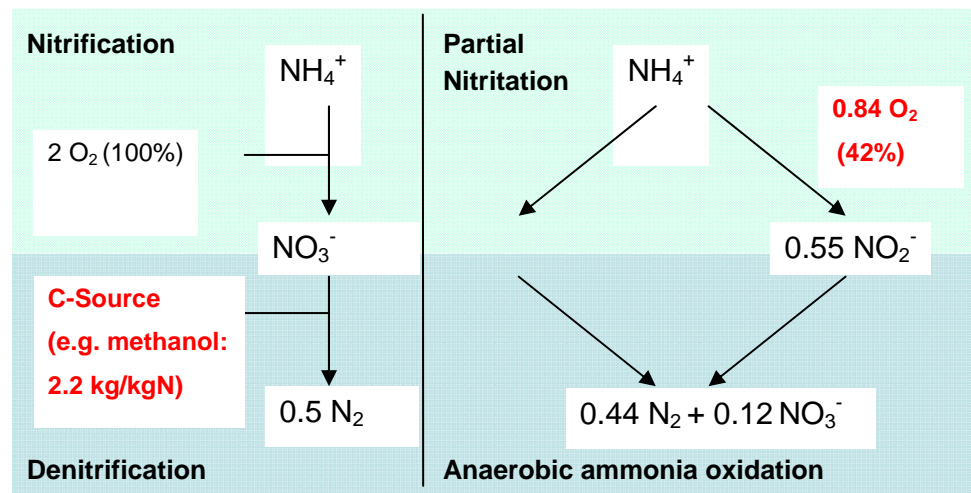


Figure 3 Comparison of ammonia removal via conventional nitrification/denitrification (left) and via partial nitrification/anammox (right). In Table 1 no NO_3^- is found in the effluent due to heterotrophic denitrification.

9.4.2 Equipment

Figure 1 shows a schematic layout of the reactor. Key elements are:

- Influent control, normally done by a pump or valve
- Reactor fill level gauge, mostly done by a differential hydrostatic pressure sensor
- Decantation unit
- Fine bubble aeration unit
- Stirring unit
- Measurement of the oxygen concentration in solution; due to the low target values and the high oxygen uptake rate this sensor must be implemented directly in the reactor (i.e. not in a bypass compartment for comfortable maintenance) and will give only an indicative measure since the oxygen concentration in the reactor is not homogeneous, since its consumption is fast compared to the reactor mixing; in some installations only the optical LDO sensor proved suitable, while gas membrane sensor was not stable
- Online ammonia sensor is used for cycle control
- Measurement of pH and conductivity are normally used for redundant checking measurements

- Since on several plants temporary foam formation was observed, it is recommended installing a device for foam controlling (sprinkler for treated water).

9.4.3 Monitoring and control

Due to the slow growth of the biomass (net doubling times between 15 and 25 days were achieved during start-up of full scale reactors), reliably avoiding toxic inhibition is of central importance for process stability. Hereto the reactor control must guarantee the following (see also section 1.2):

- By controlling the air supply, nitrite formation is limited to allow the anammox biomass to constantly deplete it, hence avoiding its accumulation; the aeration rate is manually controlled according to the offline nitrite measurement, while the measurement of O_2 in solution only serves as a redundant control to avoid oxygen reaching toxic concentration
- Reaching a set minimal ammonia concentration automatically terminates the aeration phase (e.g. $10 \text{ mgNH}_4^+-\text{N L}^{-1}$). Online ion selective ammonia sensors have been shown suitable for this purpose. Alternatively the conductivity signal may be used, since ammonia is the major ion causing conductivity change during the process. Nevertheless, to avoid long term nitrite accumulation the conductivity signal must be accompanied by offline nitrite measurement (an ion selective online electrode for nitrite is currently not available)
- The stirring phase after aeration is meant to completely deplete nitrite. Residual nitrite present in the sedimentation phase may result in nitrogen gas bubbles hampering sludge settling
- 30 to 60 minutes have been shown sufficient for sludge settling
- The pauses intercalated between cycles serve to adapt the reactor activity to the supernatant volume to be treated. Net hydraulic retention times down to one day have been shown feasible for municipal applications
- sludge withdrawal may be done actively by keeping a sludge age around 30 to 40 days or simply by limiting the sludge settling time to withdraw part of it during decantation

9.4.4 Maintenance - operational stability - safety requirements

Full scale applications have confirmed that the maintenance of the ion selective electrodes is needed roughly once per month, while control measurements should be done weekly or every second week.

The start-up and the operation of the full scale reactors as well as the preceding pilot-scale experiments (also operated over years) confirm the process as robust and stable: during the gathered experience several technical failures of equipment have occurred, without causing major problems for the operation. Biomass inhibition over hours or few days by oxygen (several $\text{mgO}_2 \text{ L}^{-1}$) or nitrite (up to $>200 \text{ mgNO}_2^--\text{N L}^{-1}$) has shown to disappear without major activity loss, after depletion of the toxicant.

9.5 COSTS

According to the data from WWTP Zurich-Werdhölzli, the total costs for nitrification/anammox sum up to €1.5 kgN⁻¹_{removed} compared to €2.5 kgN⁻¹_{removed} for conventional nitrification and denitrification with methanol: the savings sum up to 2.2 kg methanol kg⁻¹NH₄⁺-N_{removed} (corresponding to 12 kWh_{primary} kg⁻¹N_{removed}) and approximately 1.5 kWh_{electrical} kg⁻¹N_{removed} for reduced aeration requirement. The cost savings for the lowered biomass production are not included here, since dependent on the local sludge disposal. It is therefore assumed, that the new process will substitute conventional treatment as state of the art in case nitrogen removal from supernatant is required.

9.6 FULL SCALE EXPERIENCE

The five full scale reactors have been in operation since their start-up between August 2007 and July 2008. To our knowledge several follow-up projects are currently in the planning phase in Germany and Austria.

9.7 OUTLOOK AND KNOWLEDGE GAPS

Efficient deammonification of digester supernatant allows diverting more influent substrate to anaerobic digestion and herewith increase the biogas production, since the reduced ammonia load to the activated sludge compartment results in less organic substrate being required for denitrification. The WWTP of Zurich-Werdhölzli and Innsbruck have shown that this in combination with the co-digestion of industrial substrates may lead to energy autarky of municipal treatment.

The identification of toxicants is seen as an open point (e.g. specific organic compounds and COD).

The applicability of the process to ammonia rich fluids other than supernatant from digestion of municipal sludge represents another knowledge gap for wider applicability of the process.

Theoretical studies on population dynamics may allow for better understanding of the competition of different biomasses relevant for the processes and herewith maybe to improve the empirical way on how to avoid the growth of nitrite oxidizers

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10

FULL SCALE WASTEWATER OZONATION

10.1 INTRODUCTION

Ozone is a chemical oxidant and has been used since the beginning of the last century in drinking water production for different purposes. The main objective in drinking water treatment is disinfection but ozone is also used for iron and manganese removal, decolorization, control of taste and odor compounds, removal of organic micropollutants, biological stabilization and the control of chlorination by-products [1]. Ozonation is one of the promising technologies for the removal of micropollutants from wastewater [2]. Another aspect is the upgrade of bathing water quality in terms of concentration of pathogenic microorganisms in rivers with regard to the amendment of the EU bathing water directive in 2006. Hence, it is of special interest to evaluate and implement a technology combining the removal of micropollutants from wastewater with disinfection. Powdered activated carbon is promising for the removal of micropollutants but does not disinfect the water while the contrary applies to UV treatment. In contrast, ozonation has the advantage of combining these two processes. Several studies demonstrated that ozonation is an efficient treatment process for the transformation of pharmaceuticals in drinking water [2, 3] and wastewater in lab- [4, 5] and pilot-scale studies [6]. Consequently, a full scale ozonation step was successfully implemented as a tertiary treatment step at the wastewater treatment plant (WWTP) in Regensdorf, Switzerland [7, 8]. Further full scale ozonation steps are currently evaluated in different countries.

Table 1 Advantages and disadvantages of ozonation

Pros	Cons
<ul style="list-style-type: none"> • Safe and reliable full scale operation during 16 months at WWTP Regensdorf, Switzerland • Energy requirement of a typical medium-sized nutrient removal WWTP is increased only by 15% • Fast transformation of a broad spectrum of micropollutants • Good disinfection of the wastewater (<i>E. coli</i>, Total cell counts) • Combination of ozonation and sand filtration lowers the DOC • Effect based measures of micropollutants reduced by ozonation (estrogenicity, inhibition of photosynthesis) 	<ul style="list-style-type: none"> • Installation only feasible at wastewater treatment plants > 10.000 P.E. • Risk of ozone leakage into working areas • Prerequisite: efficient operation of the biological treatment step (nitrification!) • Limited transformation of some ozone-resistant micropollutants such as iodinated X-ray contrast media • Formation of oxidation by-products such as bromate, <i>N</i>-Nitrosodimethylamine (NDMA) and assimilable organic carbon (AOC) • Results from in-vivo ecotoxicity tests are controversial • A subsequent biological treatment step (e.g. sand filtration) is strongly recommended for the removal of NDMA, AOC and subtle ecotoxic effects

10.2 SCHEMATIC OUTLINE

Figure 1 shows the scheme of the full scale ozonation step at WWTP Regensdorf, Switzerland, which was installed as a tertiary treatment step. Ozone was produced on-site from liquid oxygen. The ozone-containing oxygen gas is subsequently added to the wastewater stream via gas bubble diffusers and can either be dosed flow- or DOC load proportional.

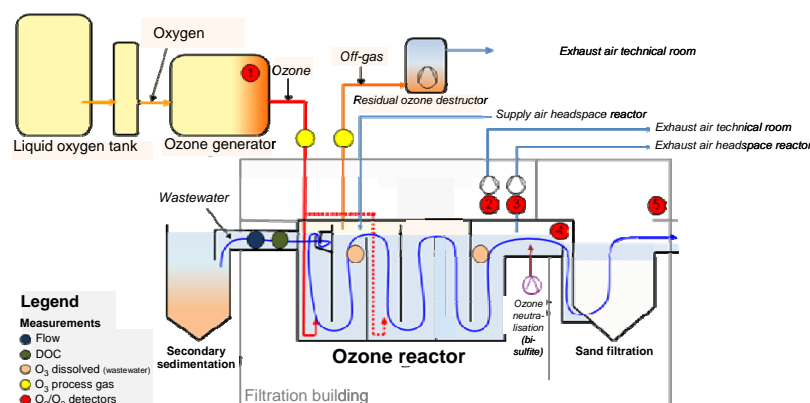


Figure 1 Scheme of a full scale ozonation after secondary sedimentation.

10.3 WATER QUALITY

Ozone can effectively oxidize micropollutants containing electron-rich moieties such as olefines (carbamazepine), amines (sulfamethoxazole, diclofenac) or activated aromatic systems, e. g., phenolic groups (17 α -ethinylestradiol) from wastewater. Thereby, oxidation only means transformation of the parent compound but not a complete mineralization. Figure 2 shows the oxidation of a selection of environmentally relevant micropollutants that were measured at the influent and the effluent of the full scale ozonation step at WWTP Regensdorf, Switzerland. Many of the compounds containing electron-rich moieties were oxidized to concentrations below the detection limit using 0.6 g O₃/g DOC. Compounds more resistant against oxidation by ozone such as atenolol and benzotriazole were increasingly transformed with increasing ozone doses. Only a few micropollutants such as x-ray contrast media (iopromide) persisted almost completely during ozonation [7, 8].

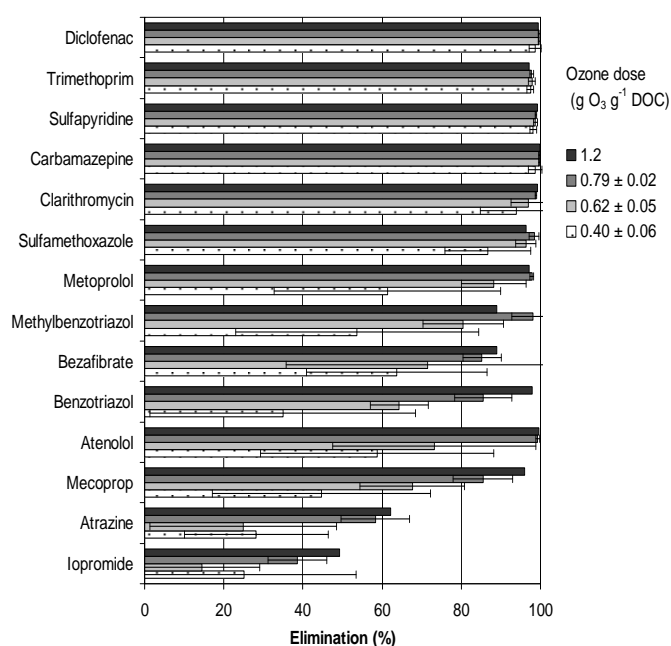


Figure 2 Effect of the ozone dose on the relative elimination of selected micropollutants during ozonation in the full scale reactor.

Concerning oxidation by-products, low concentrations of about 5-14 ng/L of the carcinogenic NDMA (a nitrosamine) were produced, but ~50 % were removed during the subsequent sand filtration [7]. Formation of the potentially carcinogenic bromate from bromide was about 7.5 µg/L at the highest applied ozone dose (1.24 g O₃/g DOC) and hence always far below the ecotoxicological guideline value of 3 mg/L and even below the drinking water standard of 10 µg/L [8]. Other organic by-products are formed from the oxidative breakdown of effluent organic matter (EOM) which are partly biodegradable and summarized as assimilable organic carbon (AOC). During ozonation, AOC was formed up to a maximum concentration of 740 µg/L but 14-46 % removed during sand filtration [8].

Concerning disinfection, the combination of ozonation and sand filtration lowered the total cell number (0.5 – 1.5 log units) as well as *E. coli* (2 – 2.5 log units) and *enterococci* (1 – 3 log units) numbers considerably. Due to the formation of assimilable organic carbon (AOC) by ozonation, a slight increase of the total cell number was observed after sand filtration in comparison to ozonation only.

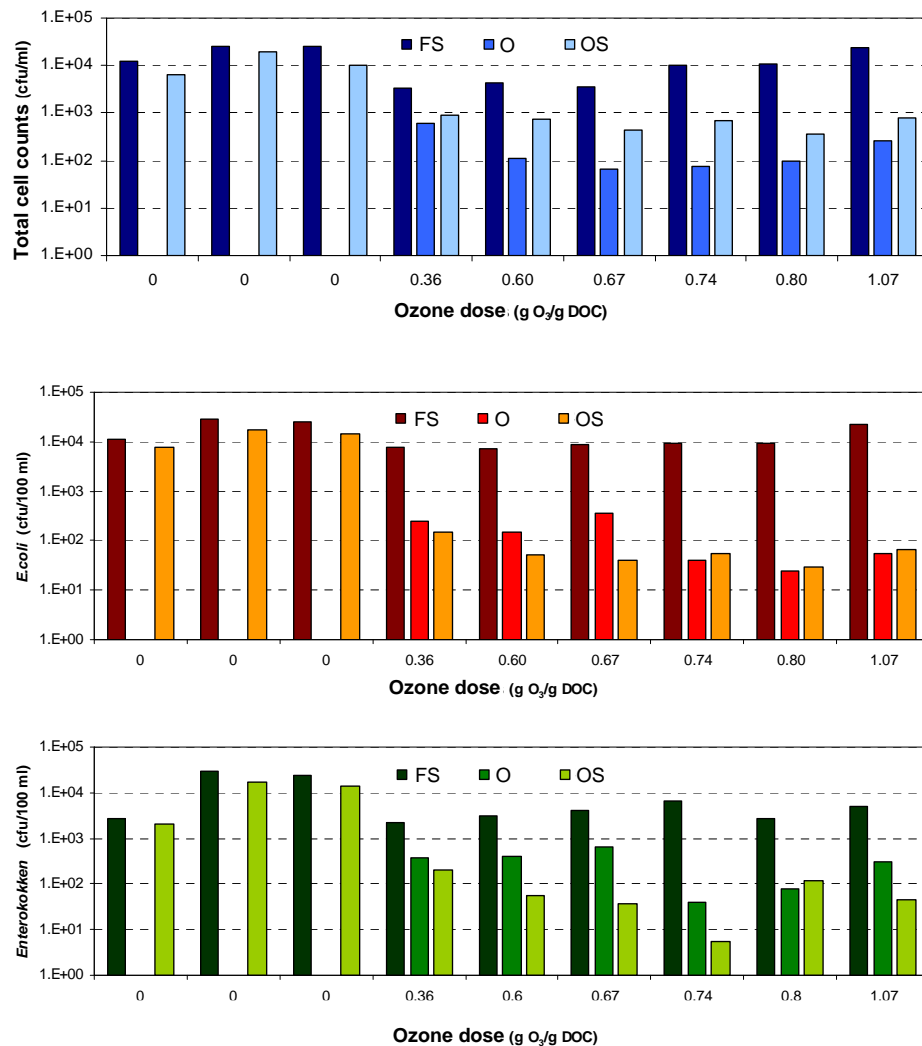


Figure 3 Inactivation of selected microorganisms [%] by sand filtration only (0 g_{O₃}/g_{DOC}) and by the combination of ozonation and sand filtration.

A strong decrease in ecotoxicity was observed with effect based ecotoxicological bioassays using enriched wastewater samples. Both specific (Acetylcholinesterase, YES and algae test) and non-specific toxicity (algae and bioluminescence test) was significantly lowered. This indicates that substances enriched prior to the bioassays and responsible for the mentioned effects were reduced significantly during ozonation (Figure 4) [9].

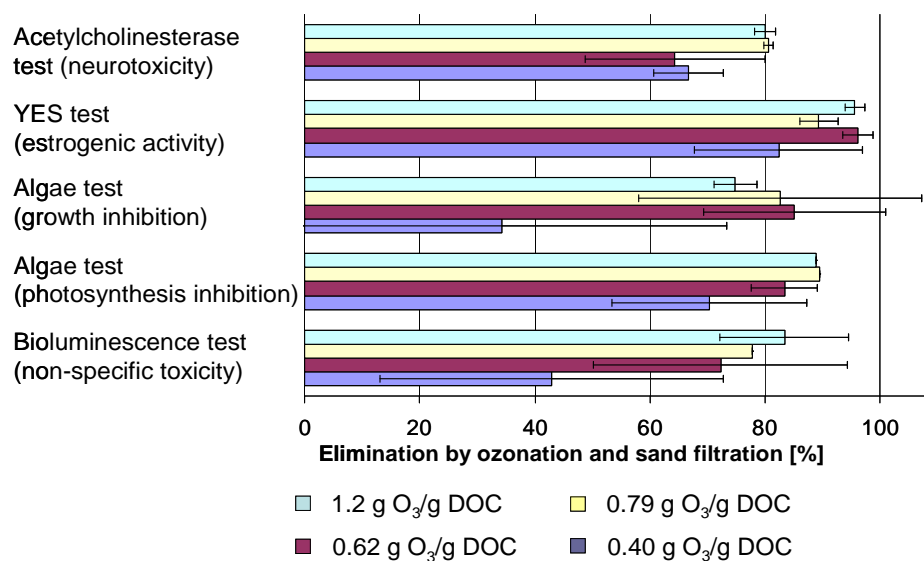


Figure 4 Elimination of ecotoxicity by the combination of ozonation and sand filtration for four different ozone doses.

However, in-vivo experiments using the early life stage test with rainbow trout (*Oncorhynchus mykiss*) eggs showed a developmental retardation (delayed swim-up and reduced biomass) after ozonation probably due to toxic biodegradable oxidation by-products. This effect was not observed after sand filtration (Figure 5). Though, vitellogenin levels of the exposed fish as a measure for estrogenicity were significantly reduced after ozonation indicating an efficient estrogenicity removal [10].

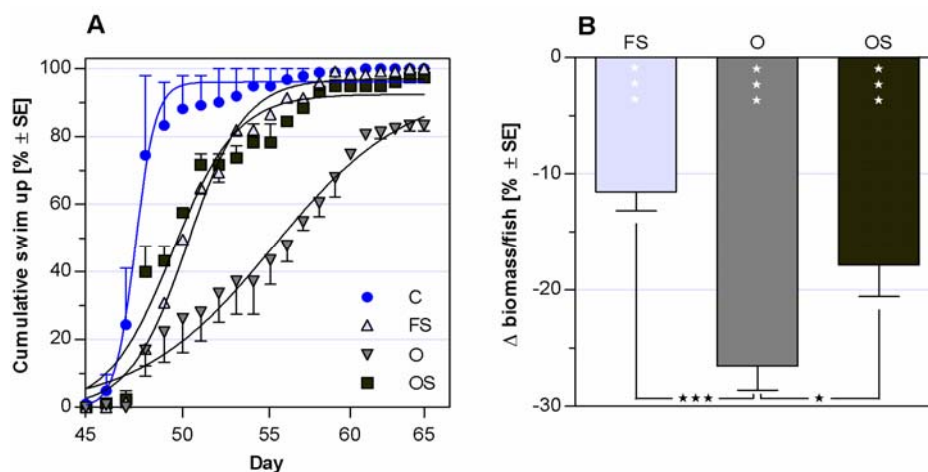


Figure 5 Cumulative swim up (A) and biomass percentage relative to control (B) of *Oncorhynchus mykiss* larvae exposed to differently treated and membrane filtered wastewaters. Abbreviations: C, control water; FS, final sedimentation; O, ozonation; OS, ozonation and sand filtration; SE, standard error. Significant differences to the control are indicated with white asterisks, between treatments with black asterisks (Kruskal-Wallis with Dunn's post Test: ★, $p < 0.05$; ★★, $p < 0.01$; ★★★, $p < 0.001$).

Hence, there is a need of clarification concerning the impact of ozonation on wastewater ecotoxicity. For example, a longer

hydraulic retention time in the biological treatment step after ozonation may further remove ecotoxicological relevant oxidation by-products. Another issue is the drinking water relevance of lowered micropollutants vs. formed oxidation by-product concentrations. Even though ecotoxicity may not change significantly, drinking water relevance should be taken into consideration as well when evaluating ozonation as a treatment technique for micropollutants oxidation.

In conclusion, the full scale reactor proves ozonation to be an efficient technique for the oxidation of a variety of micropollutants from secondary effluent as well as for disinfection. The results from ecotoxicity tests are controversial and there is an ongoing need for clarification. Bioassays using enriched wastewater samples show a significant decrease in specific and non-specific ecotoxicity while in-vivo tests with fully exposed rainbow trout eggs show only a slight improvement or no change in ecotoxicity. A subsequent biological treatment step (e.g. rapid sand filtration) is strongly recommended for the elimination of oxidation by-products which are formed during ozonation (NDMA, AOC).

10.4 PROCESS DESCRIPTION

10.4.1 Basic aspects

Ozone is a very selective oxidant, but its unique feature is its decomposition in water into OH radicals which are the strongest oxidants in water [11, 12]. Ozone is an electrophilic compound and therefore reacts faster with electron-rich compounds [11]. The OH radical, however, acts very unspecifically and is produced in relatively high yields in wastewater compared to natural waters [11, 13]. The efficiency of an ozonation process depends on the ozone dose, the ozone stability and the OH radical yield from the reactions of ozone with various reaction partners in the wastewater. The OH radical yield is especially important for ozone-resistant micropollutants. The DOC concentration of the treated wastewater, its pH value and alkalinity in turn influence the ozone stability considerably. Ozone is more stable for lower DOC concentrations, lower pH values and a higher alkalinity. Furthermore, the ozone stability is affected by the temperature, with ozone being less stable at higher temperatures.

10.4.2 Equipment

As shown in Figure 1, the following equipment is needed for a full scale ozonation step:

- Liquid oxygen tank including an evaporation station and pressure reduction valves
- Ozone generator combined with a cooling aggregate
- Diffusor elements for the addition of the ozone/oxygen gas mixture to the wastewater stream

- Sealed ozone reactor with a sufficient hydraulic retention time (10 to 20 minutes subject to wastewater chemistry)
- Residual ozone destructor for the exhaust gas
- Rapid sand filter (recommended to lower toxic oxidation by-products)
- Process measuring and control technology including online measurements for ozone dosing (flow, DOC (recommended))
- Safety: ozone and oxygen gas detectors, ozone dissolved measurement devices to monitor the ozone decay or/and residual ozone at the effluent, ozone neutralisation with bisulfite (optional)

10.4.3 Monitoring and control

Ozone can either be dosed flow- or DOC load proportional. This is achieved by holding a fixed ozone concentration in the process gas and varying the amount of process gas dosed or vice versa. Keeping the ozone concentration in the process gas between $160\text{--}180\text{ g m}^{-3}$ resulted in the lowest energy consumption ($15\text{--}16\text{ kWh/kgO}_3$) including the energy for the pure oxygen production at the full scale ozonation step at WWTP Regensdorf. During low DOC loads (e.g. night hours) the process gas concentration had to be reduced because a minimum process gas flow was required for a sufficient mixing.

In addition, a system is needed to monitor the dissolved ozone concentrations at specific points inside the reactor (optional) and at the effluent of the reactor to avoid the release of dissolved ozone to the sand filtration. At the full scale ozonation step of WWTP Regensdorf (pH 7, 5 mg DOC/L), an ozone dose of $0.80\text{ g O}_3/\text{g DOC}$ could be dosed under normal weather conditions resulting in hydraulic retention times of 7 - 8 min. In case of a higher pH or DOC concentrations, this dose will be consumed more rapidly.

The DOC online measurement was rather complicated and time-consuming. It is hence currently discussed whether ozone should better be dosed flow-proportionally while a sufficient hydraulic retention time of e.g. 10 - 20 min guarantees the complete ozone decay under all discharge conditions. This applies especially to heavy rain events, during which the flow can increase dramatically and the DOC concentrations are lowered. This results in low DOC loads increasing the ozone stability while the lowered hydraulic retention time limits the time for complete ozone decay. At WWTP Regensdorf, the hydraulic retention time in the ozonation step was decreased to 3 min under heavy rain conditions resulting in a maximum possible ozone dose of $0.30\text{ g O}_3/\text{g DOC}$.

10.4.4 Maintenance - operational stability – safety requirements

Ozone is an aggressive and toxic gas. Therefore, its concentration should be kept under the MAK value of 200 g/m^3 . It is highly important that the ozonation reactor as well as all gas pipes are fully sealed to avoid ozone release to buildings and the environment. Furthermore, all installations that are in contact with gaseous or aqueous ozone have to be made out of ozone-resistant materials. Ozone as well as oxygen gas detectors must be installed in all rooms as well as in close distance to the liquid oxygen tank. Further safety installations for the

dosage of bisulfite or H_2O_2 may be required in case the hydraulic residence time is not sufficient for complete ozone decay during heavy rain events. Since ozone gasses out from water, the headspace of the reactor must be sucked constantly towards an ozone destructor to ensure that only oxygen is released to the environment.

10.5 COSTS

Concerning energy consumption, the ozonation step was optimized during the study resulting in 0.04 kWh/m^3 wastewater at an ozone dose of $0.6 \text{ g}_{\text{O}_3}/\text{g}_{\text{DOC}}$ ($12 \text{ kWh/kg}_{\text{O}_3}$, $4\text{--}6 \text{ mg}_{\text{DOC}}/\text{L}$). Additionally, 0.02 kWh/m^3 wastewater electrical energy was needed for pure oxygen production. This corresponds to 15–20% of the total energy consumption of a conventional wastewater treatment plant ($0.3\text{--}0.4 \text{ kWh/m}^3$). Table 2 lists details for the full scale ozonation step without sand filtration. These costs may vary between countries due to different costs for energy and personnel. When taking the investment costs into account as well, the overall costs for ozonation including sand filtration were calculated to be $0.09\text{--}0.3 \text{ CHF/m}^3$ wastewater for plant sizes between 30'000–500'000 PE, respectively.

Table 2 Estimated yearly costs for the full scale ozonation step (without sand filtration) at WWTP Regensdorf, Switzerland.

		Unit
Investment (15a / 4%) ^a	155'000	CHF/a
Personnel ^b	30'000	CHF/a
Maintenance	30'000	CHF/a
Oxygen ^c	35'000	CHF/a
Energy ^d	10'000	CHF/a
Total	260'000	CHF/a
Spec. Costs (for 3 Mio. m ³ wastewater / a)	0.087	CHF/m ³ wastewater

^apayback period 15 years, linear amortization with 4 % interest

^bbased on 700 h/year internal and external personnel for maintenance of DOC sensor, ozone dissolved measurement and gas warn devices

^cbased on $0.32 \text{ CHF/kg}_{\text{O}_2}$

^dbased on energy costs of 0.086 CHF/kWh

10.6 KNOWLEDGE GAPS

The full scale ozonation step at WWTP Regensdorf already proved ozonation to be an applicable and efficient technique for the enhanced treatment of wastewater at reasonable costs. Since the pH has a large influence on the stability of ozone, it is of concern to implement a full scale ozonation step at a plant treating wastewater at a higher pH (> 7.0) as well. Furthermore, the online measurements as well as the dosing method should be carefully evaluated. Formation of oxidation by-products may differ as well for wastewater from different sources. As mentioned before, ecotoxicity and drinking water relevance of the treated wastewater should further be evaluated.

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11

POWDERED ACTIVATED CARBON

11.1 INTRODUCTION

In many areas of the drinking water-, industrial wastewater treatment and in the processing of landfill leachate adsorption with carbonaceous materials or equal resins is used since long times, to remove COD- or DOC- causing ingredients. Recently they are being used to remove micropollutants out of the biologically treated water matrix. Various studies e.g. [1] proved that using adsorption can remove a large part of these substances

An adequate adsorption material is activated carbon. It can be employed in filters as granulate or can be introduced as fine-grained powder into the wastewater.

The advantages of using powdered activated carbon (PAC) instead of granulated carbon are shown in Table 1:

Table 1 Advantages and disadvantages of PAC

Pros	Cons
<ul style="list-style-type: none">• lower costs for powdered activated carbon due to lower amounts required compared to granular activated carbon• easy to dose• dosage into the aeration tank or the WWTP effluent• temporary application if required• fast adsorption-kinetics as a result of small particle diameter• improves the settling properties of the activated sludge	<ul style="list-style-type: none">• Risk of dust formation, abrasive• low exploitation of the adsorptive capacity if not recycled to biology• the increase of suspended solids leads to contamination of the water (discharge of carbon particle): filtration step recommended• additional settling tank or membrane separation required

11.2 SCHEMATIC OUTLINE

The main focus is on the dosage of powdered activated carbon. The dosage can take place at several spots of the wastewater treatment – process.

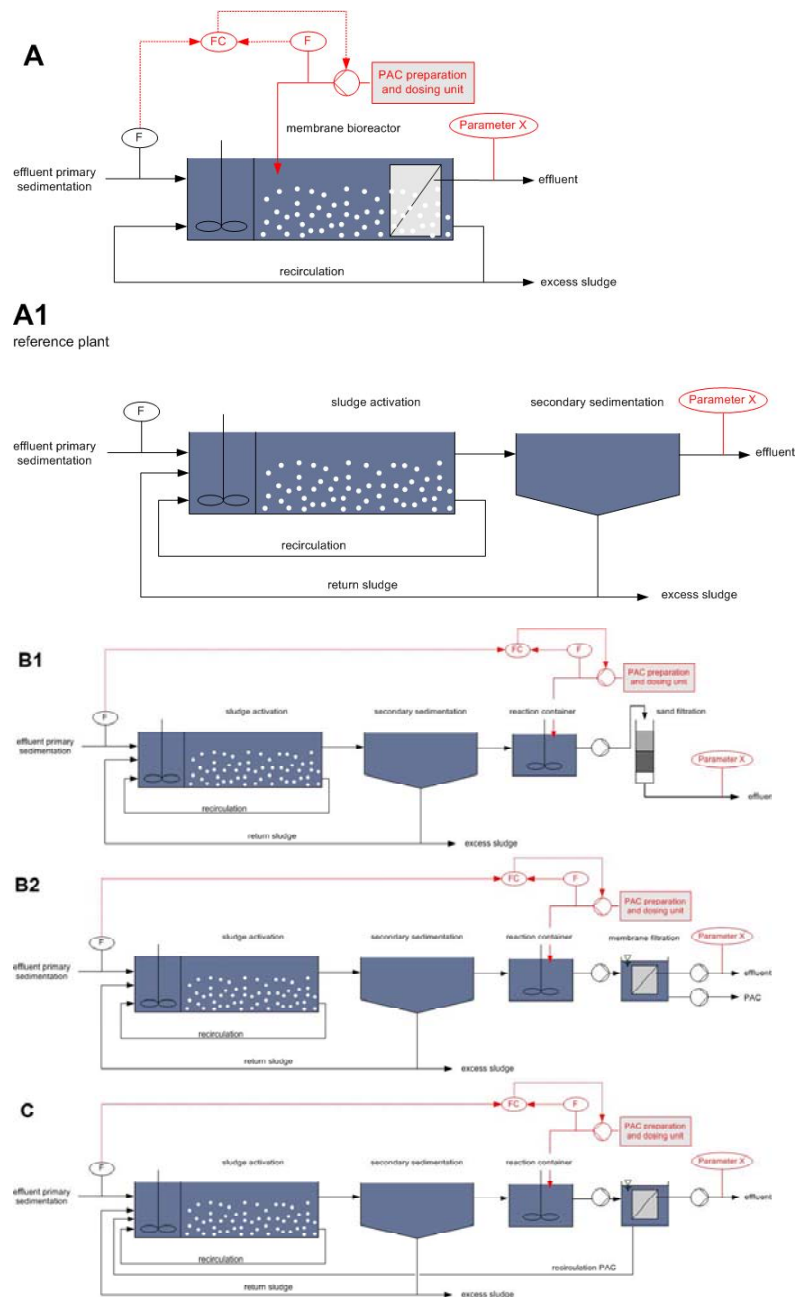


Figure 1 Schematic layout of options of dosing PAC into the wastewater treatment process: a) simultaneous adsorption in a membrane bioreactor, b) and c) Adsorption in the effluent of a WWTP with an additional filtration plant. Control units: Flow (F) and parameter to be monitored (Parameter X, individual parameter or composite parameter). PAC remains in the filter or membrane chamber for at least 1 day. Flow schemes B2 and C correspond to an option with settling tank, PAC recycling to contact tank and biology and post filtration to reduce PAC loss

The separation of the activated carbon from the treated wastewater requires an additional separation unit either in the form of sedimentation, flotation, sand filtration or a membrane, except for direct dosage into biology, which requires higher dosage. To add PAC into the effluent of a WWTP a separate coagulation- and reaction tank is needed (schematic layout B and C). In this tank the added powdered activated carbon reacts with treated wastewater. To separate the PAC from wastewater an additional separation level in the form of sedimentation, flotation, sand filtration or a membrane is required. After the settling a sand filtration or textile filtration is added to reduce PAC loss to recycling water. The application of PAC into the effluent allows recycling of the activated carbon to fully exploit its adsorptive capacity (e.g. back into the coagulations- and reaction tank and/or into the biological reactor, schematic layout C)

11.3 WATER QUALITY

Several pharmaceutical compounds with a high ecotoxicological impact have been studied. Table 2 shows the removal efficiencies at different PAC dosages and different dosage places in the wastewater treatment process.

Table 2 Elimination of selected pharmaceuticals by dosing PAC into the biological step (membrane bioreactor) respectively into the effluent of the pilot plant HtK Neuss (24h -composite sample, average)

PAC into a membrane bioreactor					
	Roxithromycin	Diclofenac	Carbamazepine	DHH	Iomeprol
20 mg PAC/L	77 %	62 %	77 %	69 %	84 %
reference (non-treated)	55 %	45 %	0 %	39 %	86 %
40 mg PAC/L	87 %	68 %	89 %	78%	76 %
reference (non-treated)	54 %	17 %	0 %	41 %	92 %
80 mg PAC/L	93 %	95 %	99 %	92 %	81 %
reference (non-treated)	39 %	28 %	0 %	18 %	92 %
PAC into the effluent (20 mg/L) with different filtration plants - additional elimination					
	Roxithromycin	Diclofenac	Carbamazepine	DHH	Iomeprol
B1: with sand filtration	68 %	49 %	88 %	50 %	33 %
B2: with membrane filtration	85 %	51 %	78 %	59 %	35 %

PAC into the effluent (20 mg/L) with recirculation into the biological step					
	Roxithromycin	Diclofenac	Carbamazepine	DHH	Iomeprol
C: membrane filtration with recirculation or PAC to biology	64 %	83 %	95 %	91 %	93 %
reference: (no PAC addition)	66 %	14 %	13 %	48 %	87 %

Activated carbon mainly adsorbs non-polar dissolved organics. The sorption behaviour strongly correlates with its octanol coefficient (K_{OW}), or with the reciprocal of its solubility in water. The K_{OW} describes the hydrophobicity of compounds. Organic substances, which are good water solvable ($K_{OW} < 3$) normally adsorbed very badly, the sorption is limited. Organic substances which are water solvable ($K_{OW} \geq 3$) rather nonpolar adsorbed well.

11.4 PROCESS DESCRIPTION

11.4.1 Basic aspects

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution.

The adsorption process can be divided into four steps:

- transport of the adsorbate (here: micropollutant) in the dilution to the border of the marginal film around the adsorbent (here: activated carbon)
- transport through the interface which surrounds the adsorbent
- transport in the inside of the adsorbent by diffusion
- 'real' adsorption of the adsorbate onto the free surface

The pH-value, the temperature as well as the sewage matrix affected the adsorption process. The adsorptive capacity/affinity of a substance is determined by its chemical-physical properties such as solubility, polarity (see above) and its concentration in the sewage.

By using activated carbon the sorbed substances is eliminated and no transformation products remain. This is a big advantage compared to oxidative processes. The contact time between active carbon and sewage in case of downstream systems should not fall below 15-30 minutes and the sludge age of the PAC in the post treatment system not below 12 - 24 hours to optimally use sorption capacity of PAC.

11.4.2 Equipment

The addition of PAC requires the following equipment:

- preparation and dosing unit (tank with level meter and stirrer, PAC silo, system)
- dosing pump
- flow measurement to control the dosage
- sampling to control the relevant parameters
- for scheme B and C: coagulation-reaction tank and additional separation units such as sedimentation, sand filtration or membranes to separate the activated carbon from the wastewater. Measurement station to control the COD, NH₄-N and NO₃-N are available on the WWTP.

11.4.3 Monitoring and control

The dosage of PAC is proportional to dry-weather-flow and effluent DOC. In this way the operation costs can be kept on a low level. In case of stormwater flow the sewage is diluted; therefore an adapted dosing of PAC proportional to the influent is not recommended.

The PAC dosing depends on the type and concentration of the target organics and the sewage composition. So are higher concentrations of PAC necessary by dosing into the biological step as by dosing into the effluent of the WWTP to reach eliminations of the same range.

11.4.4 Maintenance - operational stability – safety requirements

Maintenance:

The test duration was about 3 month for simultaneous adsorption and the application of PAC into the effluent. The experiments of PAC addition into the effluent with subsequent recirculation to biology lasted 3 weeks. During the experimental operation in half-scale no operation problems were identified. Because of the short duration of PAC dosage abrasion of pumps, gaskets etc. were not observed.

Operational stability

It is known that a municipal WWTP in Germany using a simultaneous adsorption in order to reduce AOX stopped the application of PAC because the biocenosis collapsed [2]. Within our experimental tests no change of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ effluent concentration could be observed.

Safety requirements:

For safety requirement dust formations have to be avoided. By using steam activated PAC no explosion preventions are necessary.

11.5 COSTS

Table 2 Volume flow rates taken as a basis for the cost calculations

	unit	100.000 PE
domestic wastewater Q_{a1}	$[\text{m}^3/\text{a}]$	5,475,000
municipal wastewater Q_{a2}	$[\text{m}^3/\text{a}]$	12,700,000
combined wastewater flow $Q_{m,h}$	$[\text{m}^3/\text{h}]$	2,000
dry weather flow $Q_{t,h}$	$[\text{m}^3/\text{h}]$	1,200

Table 3 Investment and operations costs for a simultaneous adsorption (20 mg PAC/L) for 100,000 PE

Investment costs	[€]	569.000
Capital costs	[€/a]	46.000
Operation costs		
Energy costs	[€/a]	8.000
	[€/kWh]	0.10
PAC costs	[€/a]	242.000
Personnel costs	[€/a]	83.000
Thermal utilisation of extra sludge	[€/a]	54.000
Maintenance (2.5 % of investment costs)	[€/a]	14.000
specific costs (€ / m ³ municipal wastewater)	[€/m ³]	0.04 (0.035)
specific costs (€ / m ³ domestic wastewater)	[€/m ³]	0.08

In total a simultaneous adsorption with 20 mg PAC/L costs €0.04 /m³ municipal wastewater respectively €0.08 /m³ domestic wastewater. Possible reductions of chemicals for sludge conditioning and sludge disposal are not included. Costs for an additional filtration plant are not included[4].

Table 4 Investment and operations costs for dosage of PAC into the effluent (20 mg PAC/L) for 100,000 PE

Investment costs	[€]	1.590.000
Capital costs	[€/a]	106.000
Operation costs		
Energy costs	[€/a]	15.000
	[€/kWh]	0.10
PAC costs	[€/a]	242.000
Personnel costs	[€/a]	83.000
Thermal utilisation of extra sludge	[€/a]	54.000
Maintenance (2.5 % of investment costs)	[€/a]	40.000
specific costs (€ / m ³ municipal wastewater)	[€/m ³]	0.04 (0.042)
specific costs (€ / m ³ domestic wastewater)	[€/m ³]	0.10

In total the application of 20 mg PAC/l into the WWTP effluent costs €0.04 /m³ municipal wastewater respectively €0.10 /m³ domestic wastewater. Here, costs for an additional filtration plant are also not included but a settling tank costs are. In literature one can find costs of operation amounting to €0.02 /m³ treated wastewater by dosing 10 mg PAC/l into the effluent [5]. The capital costs add up to €0.04 /m³ treated wastewater (contact reactor and settling tank). For this method in total costs of €0.06 /m³ are declared whereas an additional filtration step is not included. [5]

11.6 FULL SCALE EXPERIENCE

To our knowledge at the moment there is no full scale experience with a simultaneous adsorption for micropollutants removal in activated sludge system. However, application of PAC into the effluent followed by sedimentation went into operation in 2010 at WWTP Mannheim and additional full-scale plants will go in operation in southern Germany in 2010/2011.

11.7 KNOWLEDGE GAPS

In long-time tests operating problems (e.g. abrasion and corrosion) should be identified. Furthermore, the impact of the PAC application on the biocenosis has to be investigated.

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12

BioMAC

12.1 INTRODUCTION

Adsorption is the process of binding and removing substances from a solution onto an adsorbent. In water treatment, activated carbon is the most commonly used adsorbent. Activated carbon is widely used in drinking water treatment and in treatment of industrial wastewater. For municipal wastewater, there is recently an increasing interest in the use of activated carbon for its ability to remove a wide range of micropollutants, either in powdered form or as granular activated carbon. Activated carbon is seen as a valuable alternative to ozonation, as because no (harmful) transformation products are formed in contrast with ozone and other AOP's. On the other hand, in contrast to ozonation, activated carbon is not able to remove pathogens or viruses. Therefore, the BioMAC concept combines granular activated carbon with membrane filtration. Furthermore, process conditions aim for the growth of a biofilm on the activated carbon which could possibly increase the lifetime of the GAC by means of biological reactivation. The concept is patented (EP1270513) by Aquafin nv.

Table 1 summarizes the advantages/disadvantage of the BioMAC concept compared to conventional activated carbon treatment

Table 1 BioMAC concept compared to conventional activated carbon treatment

Conventional activated carbon	BioMAC
Simple lay-out => Low investment costs	Complex lay-out => High investment costs
No disinfection	Physical barrier for micro-organisms
No biological reactivation	Biofilm growth => biological reactivation (to be confirmed) and degradation of pollutants less likely to adsorb to activated carbon
Easy to operate	Requires skilled personnel
Full scale experience	No full scale experience, limited pilot scale experience

Lab scale tests have indicated that the concept could almost completely remove antibiotics and to a high extent (>80%) of most of the investigated acidic pharmaceuticals and iodinated contrast media. It is however not yet proved that the

biological activation was able to extend the lifetime of the GAC. Furthermore, a significant decrease in estrogenic and anti-androgenic activity could be illustrated.

12.2 SCHEMATIC OUTLINE

The BioMAC concept has been developed by Aquafin in cooperation with Ghent University. The concept couples an *in-situ* regenerative biological activated carbon filter with a filtration device for enhanced treatment of (municipal) wastewater.

Figure 1 illustrates the process: the BioMAC consists of two unit processes, an activated carbon tank and a membrane filtration tank.

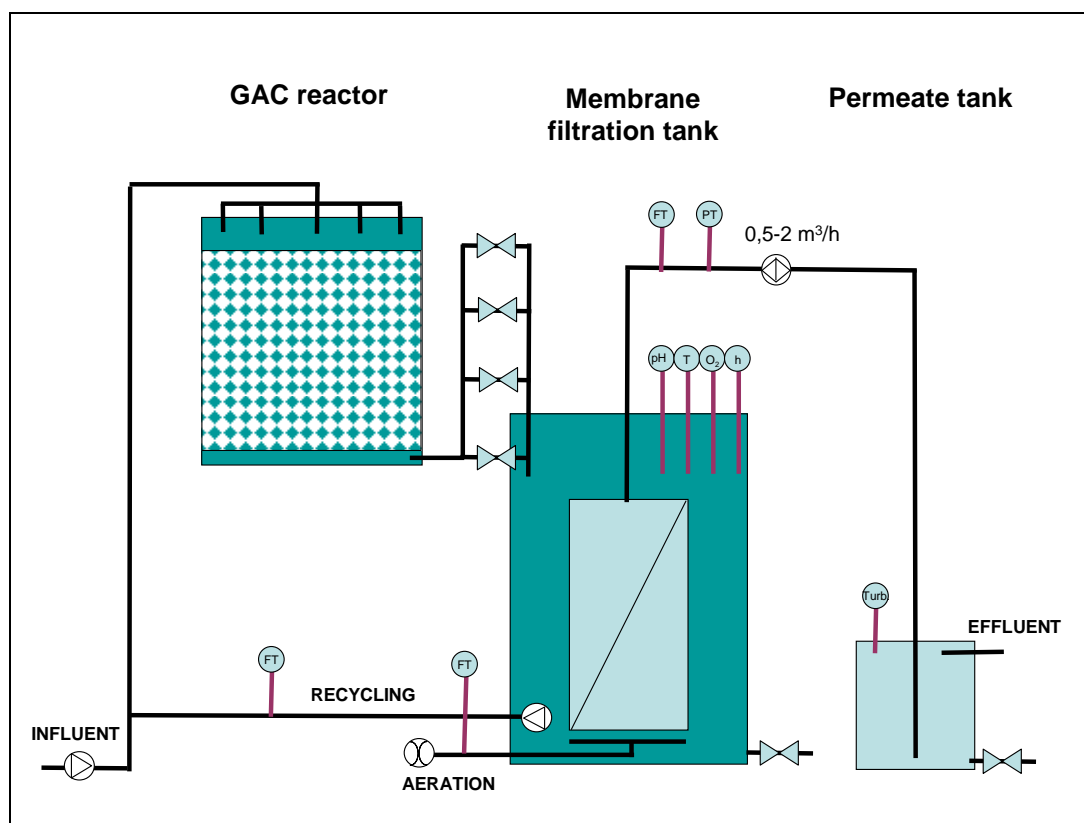


Figure 1 Set-up of the BioMAC concept

Influent (e.g. effluent from a municipal WWTP) is mixed with BioMAC retentate (recycle) and percolates through the activated carbon matrix, which is colonized by bacteria. The recycled BioMAC retentate is aerated before it is mixed with the influent in order to provide supplementary oxygen. Micropollutants present in the influent can be adsorbed to the activated carbon and/or decomposed by bacteria growing on the filter medium. This should result in an increased life span of the activated carbon.

By recycling the retentate to the activated carbon filter, the sludge retention time of the biofilm is increased and the micropollutant degrading bacteria can be maintained in the system. The effluent (filtrate) is free of suspended solids and is disinfected.

12.3 WATER QUALITY

Lab scale tests with an EBCT (empty bed contact time) of 26 minutes illustrated a good removal for antibiotics, acidic pharmaceuticals and most iodinated contrast media (Figure 2).

Tests on a pilot scale with a decreased EBCT of 13 minutes showed considerable lower removal efficiencies (limited set of results, Figure 3) for all micropollutants.

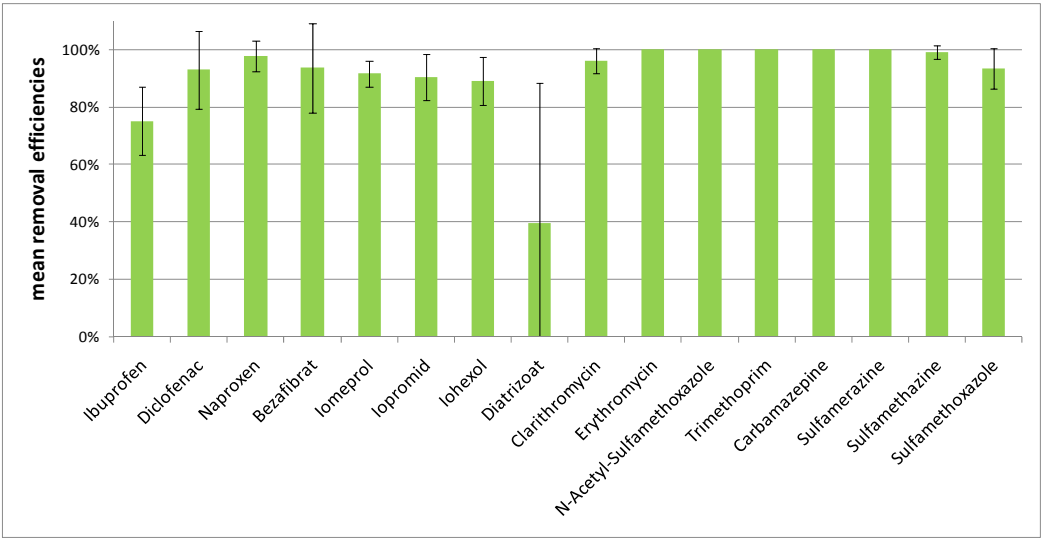


Figure 2 Removal efficiency lab scale BioMAC (EBCT = 26 minutes)

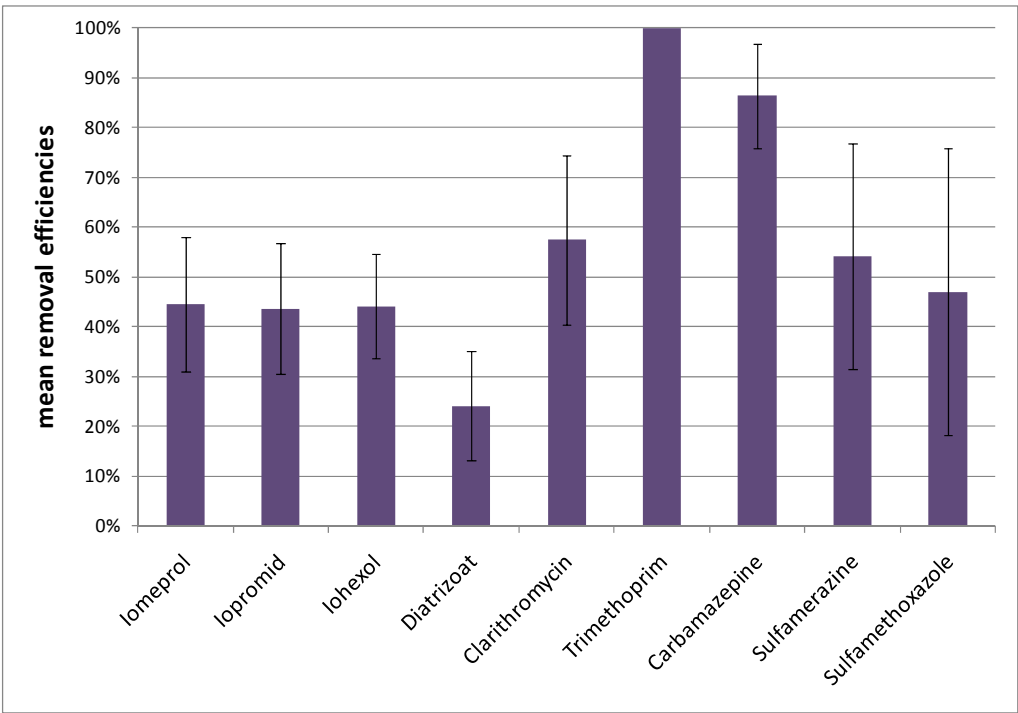


Figure 3 Removal efficiency pilo scale BioMAC (EBCT = 13 minutes)

The removal of standard parameters was not influenced by the EBCT of both set-ups. The mean concentrations for organics and nutrients are given in Table 1.

Table 1 Removal of standard parameters in BioMAC

mg/L	WWTP effluent	BioMAC EBCT = 13 minutes	BioMAC EBCT = 26 minutes
COD	28,9	12	9,9
CODfiltered	25	11,4	8,4
TOC	8,9	5,3	3,7
TOCfiltered	8,6	5,3	4
BOD	1,7	0	0
SS	8,7	0	0
NH ₄ -N	0,82	0,14	0,06
N _{tot}	7,5	6,4	5,7
Kj-N	2,6	0,9	0,8
P _{tot}	0,2	0	0,1

BioMAC treatment results in a complete removal of pathogens and a significant decrease in the estrogenic and anti-androgenic effects of the WWTP-effluent.

12.4 PROCESS DESCRIPTION

12.4.1 Basic aspects

Compounds are removed by means of adsorption, biological transformation and filtration.

Several parameters are thought to have an influence on removal efficiencies:

- temperature
- the frequency of activated carbon backwashing
- oxygen concentration
- need for aeration.

However, further research is needed to quantify the effect of these parameters.

12.4.2 Equipment

Table 2 shows the design characteristics of the pilot BioMAC designed to treat +/- 1 m³/h with an EBCT of 13 minutes.

Design characteristics		
Activated carbon		
type	-	Organosorb 10-mb
density	g/l	460
volume	l	293
weight	kg	135
mesh	-	8*30 (2.36-0.60 mm)
GAC vessel		
Diameter	m	0.67
Height	m	1.23
Height GAC in vessel	m	0.83
Membranes		
type	-	ZeeWeed 500-C
Membrane surface area	m ²	60
Filtration tank		
height	m	2.9
width	m	0.9
length	m	1.5

For an enhanced removal of pharmaceuticals, the EBCT would need to be increased to 26 minutes, which would require double the volume of the GAC tank as compared to Table 2.

12.4.3 Monitoring and control

The GAC tank is equipped with a level controller, flow meters (influent and recirculation flow) and an oxygen probe.

The membrane filtration tank is equipped for TMP (Trans Membrane Pressure) and flow measurements and level control

Other parameters that can be measured in the filtration tank, if necessary are suspended solids and nutrients

12.4.4 Maintenance - operational stability – safety requirements

Pilot scale experience led to the following conclusions regarding maintenance and operational stability:

- Depending on the concentration of suspended solids in the effluent, regular backwashing of the activated carbon is necessary to prevent clogging. An optimal backwash frequency should be determined, in order to minimise waste of the biofilm caused by the discharge of the backwash water
- The lifetime of the activated carbon in the lab scale set-up (EBCT 26 minutes) was at least 1 year. Further research is needed to confirm this.
- Membrane fluxes of 15 l/mh could be maintained without any antiscalant addition. Maintenance cleaning was needed every 8-10 weeks
- Optimal PID control of the filtration cycles is necessary to minimise membrane fouling
- The BioMAC process can easily be automated. A full-scale BioMAC plant will require rather low manpower
- BioMAC is a robust process. A plant shut-down of several days does not have an influence on future filtration stability or removal efficiencies

12.5 COSTS

Investment and operational costs for a BioMAC designed to treat an average of 50 m³/h, with maximum peak flows up to 80 m³/h, were estimated in Table 3.

Design was based on the lay-out of the pilot scale BioMAC (as in Figure 1), with an EBCT of 26 minutes.

Table 3 Cost estimation for a full scale BioMAC (50 m³/h)

Investment costs		
Construction	Tanks, piping	€ 34.340
Equipment	Pumps, electricity, blower, valves	€ 34.441
Control	Automatisation	€ 7.369

Operational costs		
Membrane replacement	Every 6 years	25.037 €/yr
GAC replacement	Yearly	29.850 €/yr
Electricity	16 kW (blower + pumps)	10.092 €/yr
Manpower	10 h/week	11.250 €/yr
Maintenance	2% investment	1.523 €/yr
Total operational cost		77.551 €/yr

Taking into account a depreciation period of 15 years, the total costs (incl. operational and investments costs) are estimated at 0,17 €/m³.

12.6 FULL SCALE EXPERIENCE

There is no full scale experience with the BioMAC concept. Operational experience has been limited to pilot scale research with a set-up treating 1 m³/h (Figure 4)



Figure 4 Pilot scale BioMAC (Aquafin, Aartselaar)

12.7 KNOWLEDGE GAPS

Further research is needed to gain more insight into

- Added value of membranes
- Lifetime of the GAC
- Influence of biological reactivation of the GAC
- Parameters influencing biological activity: backwashing of GAC, temperature
- Oxygen profile in GAC bed
- Maximum membrane flux

13

FERRATE TECHNOLOGY

13.1 INTRODUCTION

Ferrate (FeO_4^{2-}) contains Fe(VI) and exhibits strong oxidizing and disinfection properties. The unique feature of ferrate is its dual function as an oxidant/disinfectant and a subsequent coagulant since ferric ion (Fe(III)) is its non-toxic decomposition product. Several studies on the oxidation of various organic and inorganic contaminants by ferrate were reported in the 1980s and 1990s and reviewed by several authors and ferrate has gained increasing attention as a potential water treatment chemical, [1], [2], [3], [4]. Hence, some studies have focused on the ability of ferrate to oxidize single micropollutants like ibuprofen, sulfamethoxazole, carbamazepine or 17 α -ethinylestradiol (EE2), a hormone used in oral contraceptives [5], [6], [7], [8], or demonstrated that ferrate effectively decreases the estrogenic effect of EE2 (Lee et al. 2008) although it is not expected that ferrate fully mineralizes the substance. Other studies showed its ability to inactivate *Escherichia coli*, or a virus, f2 coliphage [9], [10].

Wastewater treatment plants are a point source for many anthropogenic micropollutants such as pharmaceuticals, personal care products, hormones, etc. and therefore an ideal point to lower the discharge of these compounds into the aquatic environment. Within the Neptune project, ferrate was shown to be a powerful tool to eliminate a broad range of micropollutants from water and wastewater, when these micropollutants contain electron-rich moieties (ERM), such as

- phenolic groups (e.g. EE2, E2, bisphenol A, triclosan)
- amine or anilinic moieties (e.g. sulfamethoxazole, diclofenac, enrofloxacin, ciprofloxacin)
- double bonds (e.g. carbamazepine)

Other micropollutants such as bezafibrate, iopromide or ibuprofen, that do not contain these ERMs, could be eliminated only partially even for very high ferrate doses.

Simultaneously to the micropollutants oxidation, phosphate could be removed efficiently from wastewater due to ferrate's ability to act as a coagulant [11]. Ferrate doses required for phosphate control are sufficient to eliminate the ERM-containing micropollutants. Therefore, the combined use of ferrate and Fe(III) as coagulant

could be a more economic method, since ferrate is more expensive than Fe(III).

Other oxidation technologies which are well-known from drinking water treatment, like ozonation have been shown to work efficiently for micropollutant elimination in laboratory-, pilot- and full scale studies with wastewater as well. However, in comparison to ozone, ferrate has the additional benefit of removing phosphate from wastewater which decreases the costs for other iron salts used for phosphate precipitation. In addition, in the case of ferrate it might be possible to use the infrastructure for iron dosing in flocculation filtration or post-precipitation.

13.2 SCHEMATIC OUTLINE

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 be to generate ferrate electrochemically in situ and to apply it directly for wastewater treatment (Figure 1). This approach is however, not available for large-scale production yet. Still, the application of ferrate salts is possible as well and should be carefully evaluated [12]

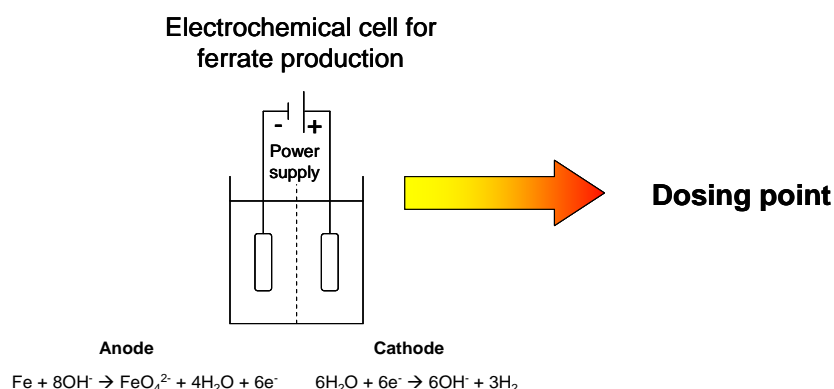


Figure 1 Scheme of an electrochemical cell for ferrate production and addition to the wastewater stream.

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 of Fe(II) and Fe(III) solutions can be used. However, technologies for on-site production of aqueous ferrate and its rapid application are required since they are not available on the market yet. Alternatively, off-site production and transport to the application site is possible as well. Figure 2 shows possible dosing points for ferrate in a wastewater treatment train. Still, addition to secondary effluent in a mixing tank (no 3) 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 2). Ferrate was consumed within >30 min in the secondary effluent without activated sludge, whereas in the wastewater with activated sludge it was completely consumed in less than 3 min. In any case, a subsequent

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

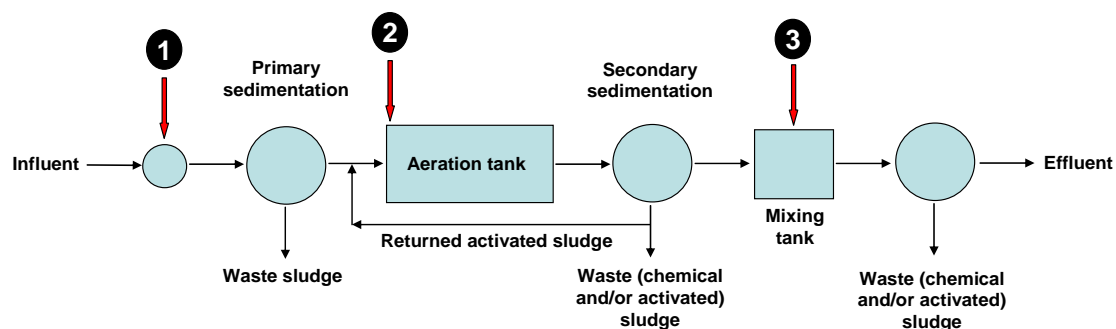


Figure 2 Dosing points for ferrate at a municipal wastewater treatment plant. For optimal use of Ferrate, dosing point 3 with additional settling or filtration unit is recommended.

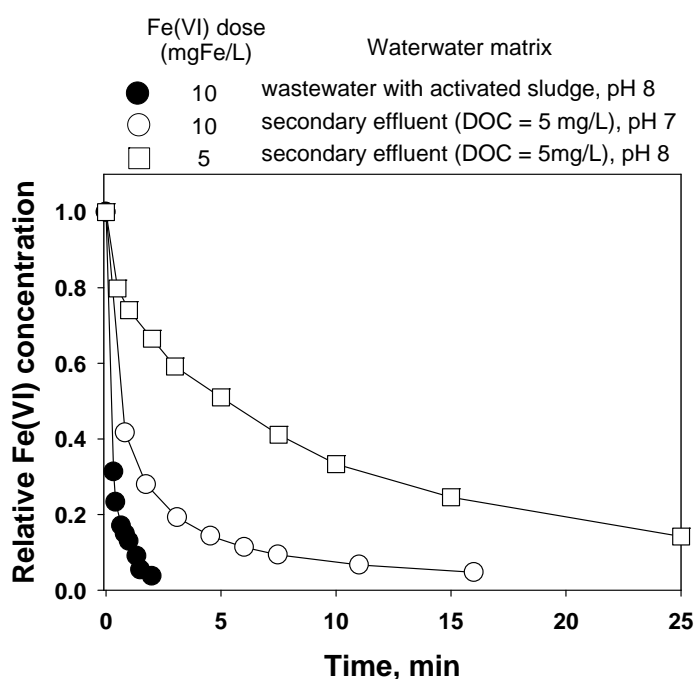


Figure 3 Comparison of Fe(VI) decreases in different wastewater matrices with and without activated sludge (corresponding to the dosing points no 2 and 3 in Figure 2, respectively). Wastewaters were taken from WWTP Dübendorf, Switzerland.

13.3 WATER QUALITY

The results shown in this section originate from laboratory experiments with secondary effluent from municipal wastewater treatment plants in Switzerland.

Ferrate efficiently oxidizes micropollutants with a chemical structure containing phenolic, amine, olefinic or other electron-rich moieties. Figure 4 shows the relative residual concentrations of different micropollutants for ferrate doses up to 5 mg Fe/L in a municipal secondary effluent. It is important to note that the relative residual concentration is concentration independent. That means, the elimination of e.g. diclofenac will always be 40 % for a ferrate dose of 1 mg Fe/L in this specific secondary effluent, independent of its starting concentration like e.g. 1 ng/L or 100 ng/L. This is true as long as diclofenac is not a major consumer of ferrate.

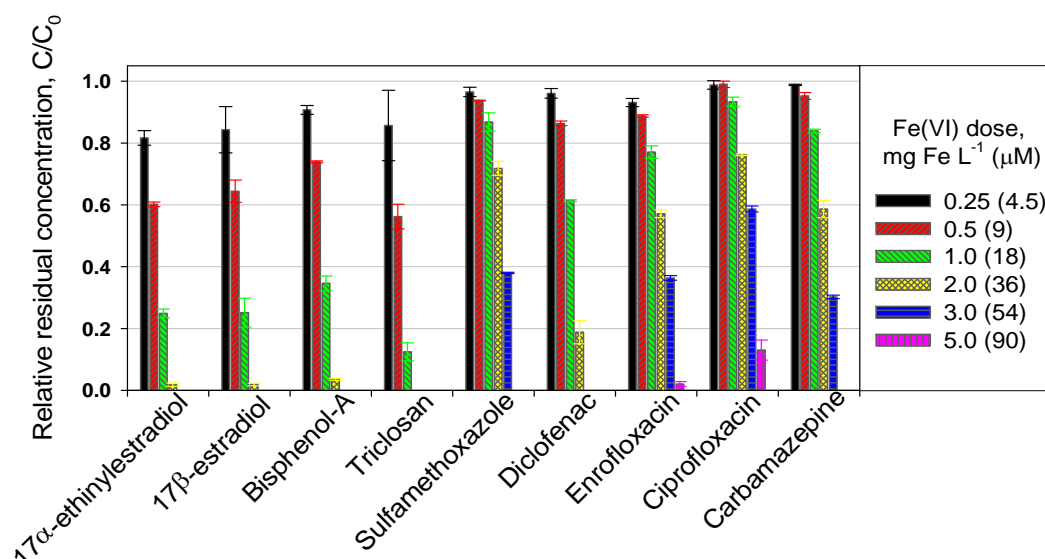


Figure 4 Relative residual concentrations of selected micropollutants during treatment of secondary effluent from WWTP Dübendorf, Switzerland, as a function of the Fe(VI) dose (0.25 – 5.0 mg Fe L⁻¹) after complete Fe(VI) consumption (3–5 hours). Experimental conditions: [micropollutants]₀ = 0.2 – 1 μM (0.05 – 0.32 mg L⁻¹), [phosphate]₀ = 3.5 mg PO₄-P L⁻¹, [DOC] = 5.1 mg C L⁻¹, pH = 7 (10 mM bicarbonate buffer), and T = 23±2 °C.

Subsequent to the micropollutant oxidation, phosphate is removed from wastewater by a ferric-phosphate precipitation (Figure 5a). The target phosphate concentrations were the Swiss regulatory limit of 0.8 mg PO₄-P/L. The necessary ferrate doses to achieve this goal (e.g. 7.5 mg Fe/L) are sufficient to fully oxidize micropollutants containing electron-rich moieties.

Figure 5b shows that Ferrate (Fe(VI)) is as efficient as Fe(II) with regard to phosphate removal and that Fe(III) is slightly less efficient compared to Fe(II) and ferrate.

The sludge generated by iron addition as post-treatment is very rich in phosphorus, and therefore suitable for nutrient recycling into agricultural fertilizer.

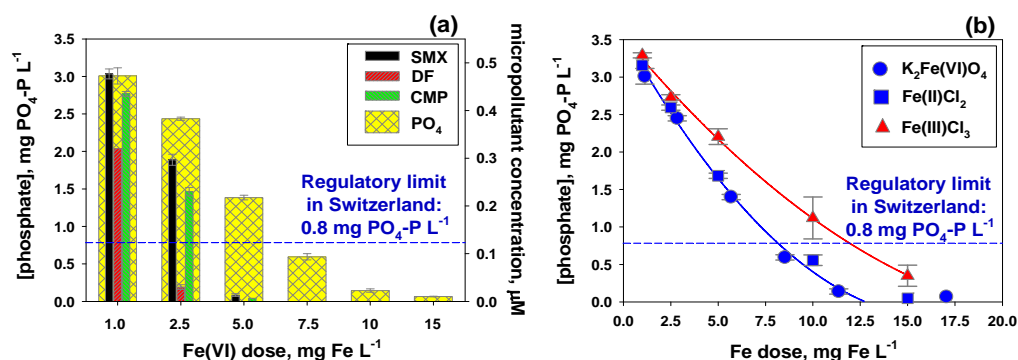


Figure 5 (a) Oxidative elimination of selected micropollutants and subsequent removal of phosphate during treatment of secondary effluent from WWTP Dübendorf, Switzerland, as a function of the Fe(VI) dose (1.0 – 15 mg Fe L⁻¹)

Figure 5(b) comparison of phosphate removal efficiency for various forms of iron. Experimental conditions: [micropollutants]₀ = 0.5 – 1 μM, [phosphate]₀ = 3.5 mg PO₄-P L⁻¹, [DOC] = 5.1 mg C L⁻¹, pH = 7 (10 mM bicarbonate buffer), and T = 23±2 °C. SMX = sulfamethoxazole, DF = diclofenac, CMP = carbamazepine.

Lee et al. 2008 [13] showed that ferrate efficiently removes estrogenic activity from wastewater containing steroid hormones and that the decrease was linearly proportional to the decrease of EE2 as a representative steroid hormone.

Furthermore, the ability of ferrate to oxidize micropollutants was tested compared to ozone, which is another promising oxidant for tertiary wastewater treatment. Figure 6 shows that in terms of micropollutant oxidation, ferrate is as or slightly less efficient than ozone on a similar molar oxidant dose. However, ferrate has the benefit of phosphate removal.

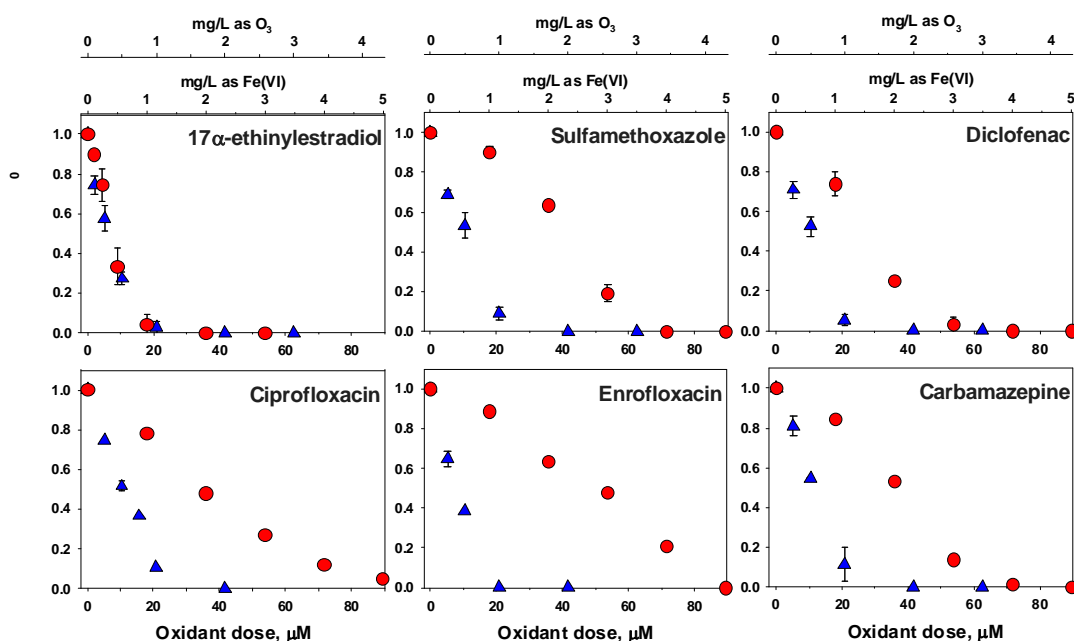


Figure 6 Comparison of the relative residual concentration after oxidation of selected micropollutants by Fe(VI) (red circles) and O₃ (blue triangles) as a function of the oxidant dose in secondary effluent from WWTP Dübendorf, Switzerland. Experimental conditions: [micropollutants]₀ = 0.2 – 1 μM (0.05 – 0.32 mg L⁻¹), [DOC] = 5.0 mg C L⁻¹, pH = 8 (20 mM borate buffer), T = 23±2 °C.

13.4 PROCESS DESCRIPTION

13.4.1 Basic aspects

Ferrate is unstable in contact with water and oxidizes micropollutants and the wastewater matrix in a first step. Furthermore, it undergoes a self-decay which can be minimized but not completely avoided by using low ferrate concentrations and by keeping the pH as high as possible. The consumption by the wastewater matrix can be minimized by applying ferrate as a tertiary treatment to secondary effluent (e.g. flocculation filtration or post-precipitation unit composed of a contact tank and sedimentation-filtration). While oxidizing organic matter and self-decaying, ferrate (Fe(VI)) is reduced to ferric ion (Fe(III)) which subsequently leads to a ferric-phosphate precipitation. After addition to the wastewater stream, it should quickly be mixed with the wastewater to enhance its efficiency. Figure 7 gives an overview on the process reactions.

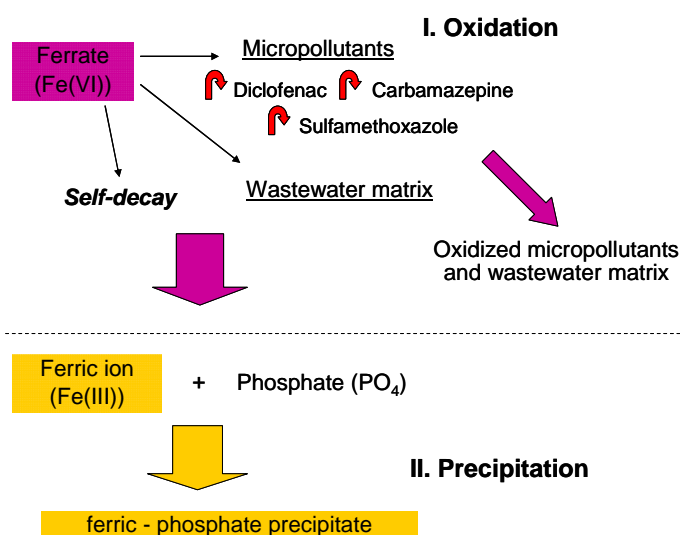


Figure 7 Process reactions of ferrate in wastewater.

13.4.2 Equipment

Pumping and mixing devices already used for the addition of iron salts can also be used for ferrate addition. In case of on-site production of ferrate by an electrochemical method, an electrochemical cell needs to be installed (see Figure 1). If stable ferrate salts were used, a mixing device as well as a storage room is needed.

13.4.3 Monitoring and control

Ferrate may be added similar to Fe (II) or (III) salt addition. 5 mg Fe/L were sufficient to fully eliminate reactive micropollutants and 7.5 mg Fe/L did lower the phosphate concentration below the Swiss standard. Hence, we recommend to dose e.g. 5 mg Fe/L effluent to fully control micropollutants concentrations and to achieve further phosphate precipitation by the addition of Fe (III) salts, when starting from an

influent phosphate concentration of ~3.5 mg PO₄-P/L.

13.4.4 Maintenance - operational stability – safety requirements

Information on potassium ferrate as a pure chemical from its safety data sheet (Sigma Aldrich) is given below:

Hazards identification

Risk advice to man and the environment

Contact with combustible material may cause fire.

Fire-fighters measures

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters

Wear self contained breathing apparatus for fire fighting if necessary.

Further information

Use water spray to cool unopened containers.

Accidental release measures

Personal precautions

Avoid dust formation. Ensure adequate ventilation. Evacuate personnel to safe areas.

Methods for cleaning up

Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

Handling and storage

Handling

Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - no smoking. Keep away from combustible material.

Storage

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

Store under inert gas. Moisture sensitive.

Potential Health Effects

Inhalation May be harmful if inhaled. May cause respiratory tract irritation.

Skin May be harmful if absorbed through skin. May cause skin irritation.

Eyes May cause eye irritation.

Ingestion May be harmful if swallowed.

Further safety requirements may apply in case ferrate is produced on-site by an electrochemical cell.

13.5 COSTS

Since large-scale production of ferrate does not exist yet, high-purity ferrate salts for laboratory use are currently expensive and cost about 100 times more than ozone. Still, because results for its application for wastewater treatment are very promising, different production technologies should be evaluated. From experience with other chemicals, costs may drop by a factor of 50 to 100 if produced as a high volume chemical. Therefore, in future the costs for ferrate might be similar to ozone (€0.06 /m³ wastewater, including both operational and investment costs).

13.6 FULL SCALE EXPERIENCE

Only laboratory-scale experience is currently available.

13.7 KNOWLEDGE GAPS

Ferrate treatment of municipal wastewater should be tested in pilot-scale plants. Furthermore, the costs for up-scaling of ferrate production including the production as stable salts and as an on-site production should be evaluated.

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14

BIOMETALS

14.1 INTRODUCTION

Biogenic metals are biologically formed metal precipitates on the cell wall of a bacterium (Figure 1). Biogenic metals have oxidative or catalytic properties and can be used for the removal of micropollutants from secondary effluent among other remediation applications [1]. Hennebel and coauthors discussed the precipitation of biogenic manganese and iron species and the microbial reduction of precious metals, such as palladium, platinum, silver and gold, with specific attention to the application of these biogenic metals in innovative remediation technologies for advanced water treatment. In this fact sheet, the focus is on biogenic manganese oxides (BioMnOx) for the oxidative removal of pharmaceuticals and biocides and on biogenic zero valent palladium (BioPd) as a catalyst for the reductive dehalogenation of iodinated X-ray contrast media (ICM).

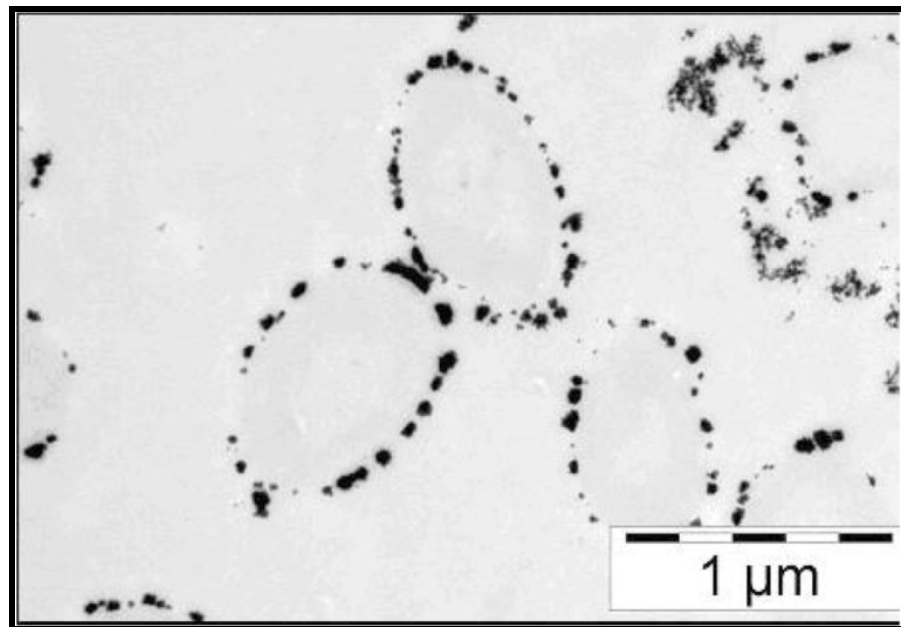


Figure 1 Transmission electron microscopy picture of bacteria with zero valent palladium nanoparticles on their cell walls

14.2 SCHEMATIC OUTLINE

Through the application of BioMnOx and BioPd as a post-treatment, micropollutants can be removed from the secondary effluent in a relatively clean matrix, thus avoiding inhibition from the matrix. The drawback of the secondary effluent is the low assimilable carbon content, which is not sufficient to support the growth of manganese-oxidizing bacteria (MOB) present in the BioMnOx. Therefore it is suggested to apply BioMnOx earlier in the treatment train of wastewater (Figure 2). The primary influent contains higher concentrations of BOD to support the growth of MOB. The use of BioPd between the denitrification and nitrification step has two advantages over BioPd as post-treatment. The anaerobic conditions after denitrification favour the *in situ* production of H₂ gas from formate or another H-donor and the most efficient way to charge the BioPd-catalyst with H for the dehalogenation reaction of the iodinated contrast media is with H₂ gas. A second advantage of the early application of BioPd in the treatment train is the subsequent putative oxidation of the carbon skeleton of the deiodinated contrast media in the nitrification tank.

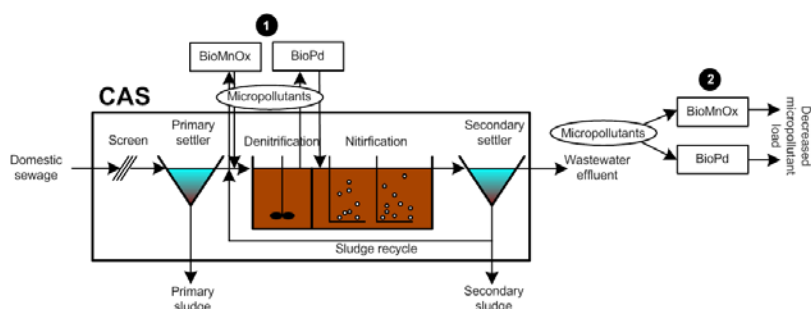


Figure 2 Sites of application of BioMnOx and BioPd within a WWTP

14.3 PROCESS DESCRIPTION

14.3.1 Basic aspects

Manganese ions (Mn(II)) can be oxidized to Mn(IV) by MOB such as *Pseudomonas* or *Leptothrix* species. *Pseudomonas putida* is a heterotrophic bacterium, easy to cultivate on glucose as a carbon source. *P. putida* rapidly oxidizes Mn(II). The biologically oxidized manganese precipitates as MnO₂ on the cell wall of the bacteria. This unique combination of the active *P. putida* and MnO₂ is called BioMnOx (Figure 3). Biologically produced manganese oxides were 10 times more reactive with micropollutants such as diclofenac than chemically produced MnO₂ [2]. The main advantage of BioMnOx over chemical MnO₂ is the ability of the bacteria to re-oxidize the formed Mn(II), thus removing the inhibiting effect on the process since the chemical oxidation of diclofenac is strongly inhibited at Mn(II) > 0.7 mg L⁻¹. In this way, the oxidation process with manganese oxides is faster and the oxidant is biologically regenerated. In Figure 3, the re-oxidation of the reduced

manganese and the ability of the manganese oxidizing bacteria to further remove the biodegradable oxidation products, are illustrated.

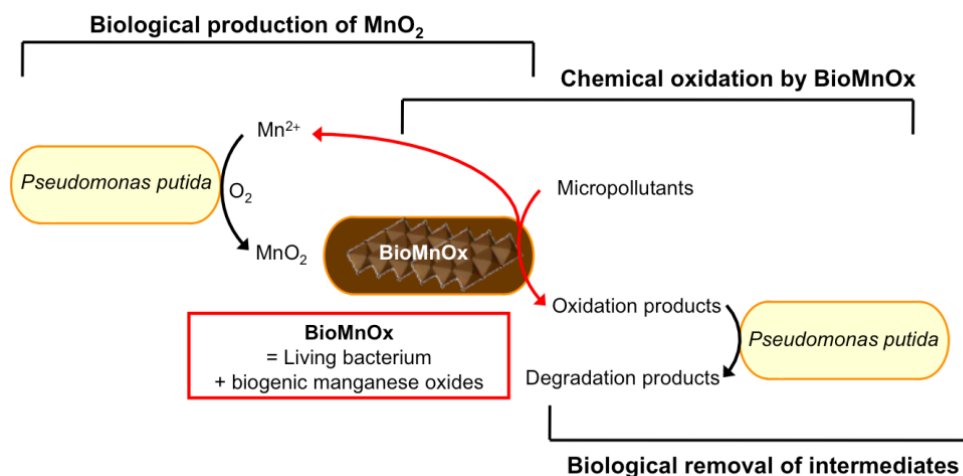


Figure 3 Schematic view of the production of biogenic manganese oxides with *Pseudomonas putida*, the chemical oxidation of pharmaceuticals with BioMnOx, the re-oxidation of the formed Mn(II) during this process and putative partial mineralization of the biodegradable oxidation products.

Pd(0), mainly in the form of nanoparticles, has been demonstrated as a highly effective catalyst for the remediation of chlorinated solvents, PCB's and other halogenated compounds in sludge and groundwater [3]. Nanocatalysts demonstrate high reactivity in reduction reactions based on their large specific surfaces. A new biologically inspired method to produce a nanopalladium catalyst is the precipitation of palladium on a bacterium, i.e. BioPd. In an anaerobic environment, the cells can reduce Pd(II) and subsequently precipitate it as Pd nanocrystals on their cell wall and in their periplasmic space (Figure 4). Mainly two model organisms are used in this production process: the metal-respiring bacterium *Shewanella oneidensis* [4] and *Desulfovibrio desulfuricans* [5]. The bacteria also serve as the stabilizer since they represent a barrier for the aggregation of the Pd nanoparticles. The reactivity of Pd and BioPd towards many halogenated groundwater and soil pollutants, such as chlorinated solvents [3] and polychlorobiphenyls [6], has been reported. The use of Pd or BioPd for the dehalogenation of pharmaceuticals such as iodinated contrast media was shown by Knitt et al. [7], Hennebel et al. (2009c), Forrez et al. [9]. In the presence of a H-donor (H_2 or $HCOOH$), Pd(0) nanoparticles are charged with molecular hydrogen, which subsequently reduced halogenated compounds (Figure 4).

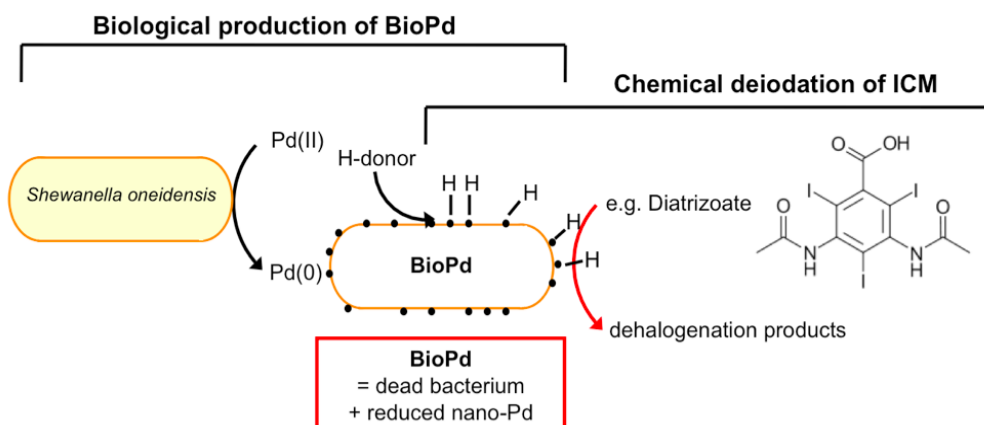


Figure 4 Schematic view of the production of bio-palladium (BioPd) with *Shewanella oneidensis*, the addition of H-donor to charge the catalyst BioPd and the chemical dehalogenation of pharmaceuticals with BioPd.

14.3.2 Configuration

Continuous outside-in operation of a submerged lab scale membrane bioreactor (MBR) with BioMnOx (Figure 5) 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 outside the MBR (Figure 5) or directly in the MBR (probable layout for full scale application).

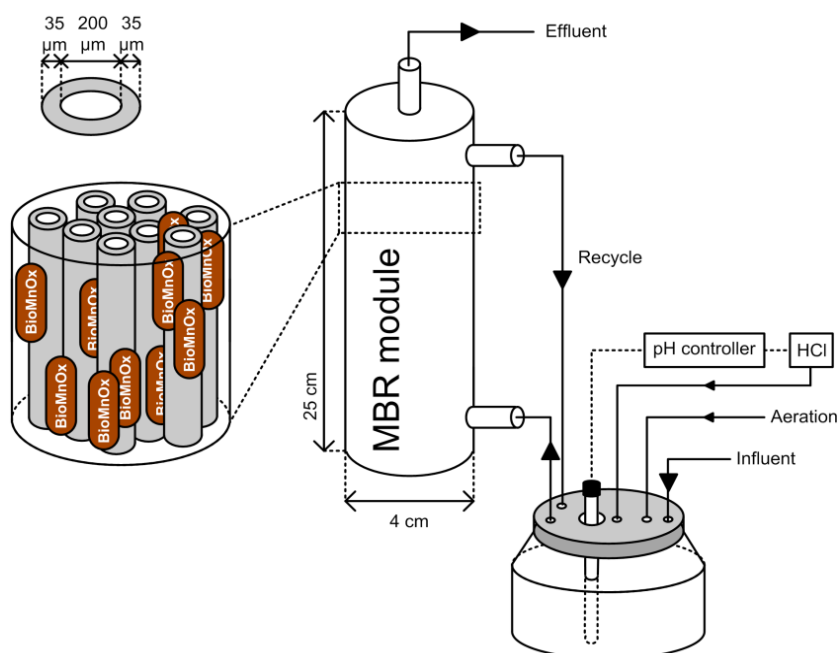


Figure 5 Configuration of the MBR with the BioMnOx hollow fibre module (200 mL) and aeration vessel (150 mL). In this configuration, aeration was applied outside the MBR and influent was introduced in the aeration vessel.

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.

Successful dehalogenation of diatrizoate has been shown by Knitt et al. [7] with chemical Pd and by Hennebel et al. (2009c) with BioPd. In the Neptune project, we demonstrated that this is also possible in a continuous way at environmental concentrations. A similar reactor set-up with hollow fibre membranes was used as with BioMnOx (Figure 5), without the pH control and the aeration. The removal of 4 ICM (diatrizoate, iomeprol, iopromide and iohexol) from WWTP-effluent occurred at environmental concentrations by more than 96%. The challenge remains in the supply of the H-donor to charge the catalyst. Formate as a hydrogen donor gave variable results ranging from 30-90% diatrizoate removal, while excellent ICM removal was obtained with biological *in situ* production of H₂.

14.3.3 Application status

Up till now BioMnOx and BioPd for micropollutant removal were only tested as a post-treatment. As mentioned in the schematic outline, BioMnOx and BioPd application earlier in the treatment of domestic wastewater could be an advantage.

The application of BioMnOx was tested in a continuous way on WWTP-effluent by using a MBR-hollow fibre-module. The next step to go to pilot or full scale application would include testing the BioMnOx in a slow sand filtration set-up. 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 MOB would benefit from the bioavailable carbon source for growth, biodegradation and

manganese-oxidizing activity.

The removal of the ICM diatrizoate was tested in a membrane contactor with BioPd immobilized in a polyvinylidene fluoride (PVDF) membrane (Hennebel et al., 2009c). And WWTP-effluent was treated in a hollow fibre MBR with BioPd in the outer compartment on lab-scale for the removal of a mixture of ICM. The BioPd technology has also been tested on a pilot-scale, not for the removal of micropollutants, but for the removal of chlorinated solvents. A plate membrane bioreactor (20 L) for the catalytic dechlorination of trichloroethane was tested successfully [3]. As a new alternative method to retain BioPd in a reactor, BioPd was immobilized in a porous matrix to form BioPd beads. The application of these beads for hexachlorocyclohexane remediation was tested on a pilot-scale fluidized bed reactor (200 L) in cooperation with LabMET, Bauer Umwelt GmbH and Avecom [11]. Application of BioPd in a sediment slurry reactor together with a source of reducing equivalents resulted in dehydrochlorination of chlorinated PCBs [6].

14.4 COSTS

The following indications are based on preliminary results on lab scale; these are clearly very coarse, and are meant only to give an order of magnitude for assessing the basic feasibility.

The hollow fiber MBR contained 14 g CDW L⁻¹. As in a plate membrane MBR, relative high biomass concentrations are applied (8-10 g CDW L⁻¹). If an axenic culture of manganese-oxidizing bacteria would be used, the cost would be as high as €14,000 (14 kg m⁻³ x €1000 kg⁻¹, the overall estimated cost of axenically produced microbial biomass) which is 10 times the cost for the membranes alone (€100 m⁻²; Gander et al., 2000; Hennebel et al., 2009c). By using a mixed culture, enriched from natural environments, the cost would be reduced considerable because no axenic conditions nor an expensive growth media is required. For the latter, Mn(II) left in the groundwater after sparging with air to selectively remove iron, could be used. For the biomass production, inoculation with surface water would be sufficient as a source of manganese-oxidizing bacteria since they are ubiquitously in the environment. To enrich for MOB, a high Mn(II) concentration gives them a growth advantage.

Minimal HRT tested in the lab were 5 h, therefore further optimization should focus on decreasing the HRT. The latter can be obtained by increased mass transfer and increase the concentration of Mn(IV) in the reactor.

The use of biogenic metals such as Bio-Pd include an additional cost for the metal itself (Pd is rather expensive (€3500 kg⁻¹) and the production of axenic biomass (€1000 kg⁻¹ bacterial cell dry weight; Hennebel et al., 2009c). Application of Bio-Pd for the reductive removal at this stage is too expensive, but effort are made to decrease the costs by developing new production approaches [13].

14.5 KNOWLEDGE GAPS

The two key features of BioMnOx are (1) the biogenic precipitated MnO_2 on the bacterial cell wall and (2) the presence of 'living' MOB. The latter is important to re-oxidize the formed Mn(II) , to remove its inhibitory effect on the oxidation reaction of the pollutant and to prevent the loss of the oxidant. MOB 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. Ways to ensure the BioMnOx activity in low carbon environments on the long term are still under development.

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

In non-buffered systems at lab-scale, 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 may be required.

For the removal of ICM by BioPd, the main challenge lies in the engineering of this *in situ* H_2 production at environmental temperatures. Other biological processes such as autohydrogenotrophic denitrification [14], hydrogenotrophic methanogenesis [15] or homoacetogenesis [16] can compete for the H_2 , which explains why a high HRT had a negative effect on this application.

Further investigation is necessary to apply BioMnOx in a slow sand filter as a low cost treatment with special attention to carbon supply for the manganese-oxidizing bacteria and pH control. The BioPd immobilized in membranes is a promising technology for the catalytic dehalogenation of micropollutant and further research is necessary for the supply of H_2 as a H-donor to charge the BioPd catalyst.

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15

NITRIFIER ENRICHED CULTURE (NEC)

15.1 INTRODUCTION

Hormones, antibiotics, pain killers, antidepressants, chemotherapy drugs, UV-filters, hair dyes, fragrances, biocides and vulcanisation accelerators are examples of compounds that are not removed completely by a biological wastewater treatment plant (WWTP; [1]). Nevertheless, there are indications that by adjusting the operation of a WWTP, the removal of micropollutants can be optimized. The parameter sludge retention time (SRT) seems to play a crucial role in the removal of pharmaceuticals and personal care products. A minimal SRT of 10 days was reported for the removal of bisphenol-A, ibuprofen, bezafibrate and the natural and synthetic estrogens [2]. To obtain a removal of more than 80%, an SRT of 5-15 days is sufficient for most micropollutants, such as the disinfectant triclosan and the UV-filter benzophenone. A smaller group of compounds (e.g. the musk fragrance galaxolide and the flame retardant TCEP) need a higher SRT of more than 15 days to obtain 80% removal [3]. In general, higher SRTs in WWTPs are related to the requirements for nitrogen removal (nitrification/denitrification).

15.2 SCHEMATIC OUTLINE

A high SRT and low loading rate can improve the biodiversity of the activated sludge, which increases the possible degradation pathways. This was shown by the significant removal of beta-blockers and psychoactive drugs at an elevated SRT of 18 days [4]. Nitrification requires normally a SRT of 15-18 days because of the low doubling time of the nitrifiers. The role of nitrification for micropollutant removal is clearly shown for the endocrine disrupting compounds (EDCs; [5]). Research with a membrane bioreactor (MBR) containing sludge enriched for nitrifiers was tested as a polishing step for the removal of EDCs. This nitrifier enriched culture (NEC) was able to remove 17α -ethinylestradiol efficiently at ng L^{-1} levels, with a minimal input of $1 \text{ mg NH}_4^+-\text{N L}^{-1}$ to ensure nitrification [6]. This shows that NEC technology can be applied as a polishing step to remove residual estrogenicity from secondary effluent.

Nitrification as a post-treatment step for WWTP-effluent allows the enzymes to work in a less polluted matrix and therefore the micropollutants are well targeted. 17 α -ethinyloestradiol (EE2) removal at high (52.5 mg NH₄⁺-N L⁻¹) and low (1.5 mg NH₄⁺-N L⁻¹) ammonium concentration showed a delay in the linear removal. The enzyme ammonium mono-oxygenase (AMO) that catalyses the EE2/NH₄⁺ co-metabolism will react first with the amount of NH₄⁺, present in much higher concentrations.

An alternative approach would be to optimize the nitrification step during the wastewater treatment by applying a SRT of minimally 15 days and a HRT of more than 8 hours. If the HRT is high enough in the aeration tank, there is enough time for the enzymes to react with the EDCs after completion of the nitrification. Inoculation from a NEC-reactor cultivating nitrifiers at low NH₄⁺-N concentration can increase the level of enzymes. At low N concentrations higher density of ammonia mono-oxygenase can be obtained, i.e. 25% instead of 7% of the protein content [7]; [8]. In Figure 1, the points in the wastewater treatment where nitrification can be applied or optimized for micropollutant removal are indicated.

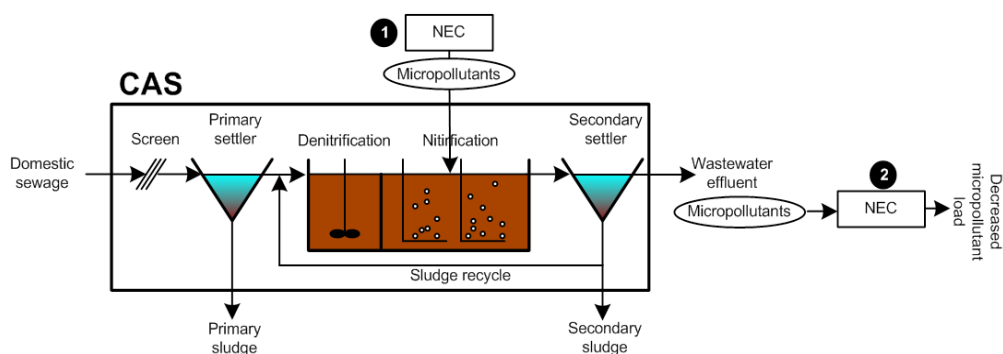


Figure 1 Application of Nitrifier Enriched Culture (NEC) in a WWTP for enhanced micropollutant removal

15.3 PROCESS DESCRIPTION

15.3.1 Basic aspects

Vader and co-workers (2000) were among the first to point out the removal of 17 α -ethinyloestradiol (EE2) by sludge with high ammonium-oxidizing activity. The enzyme AMO, responsible for the first step from NH₄⁺ to NH₂OH during nitrification, is able to catalyse the EE2/NH₄⁺ co-metabolism [9]. The enzyme AMO is intracellular and is located on the intracytoplasmatic membrane of the ammonia-oxidizing bacteria (AOB). The binuclear copper sites play a role in the oxygenation process of the pollutant as illustrated in Figure 2 with 17 α -ethinyloestradiol as an example.

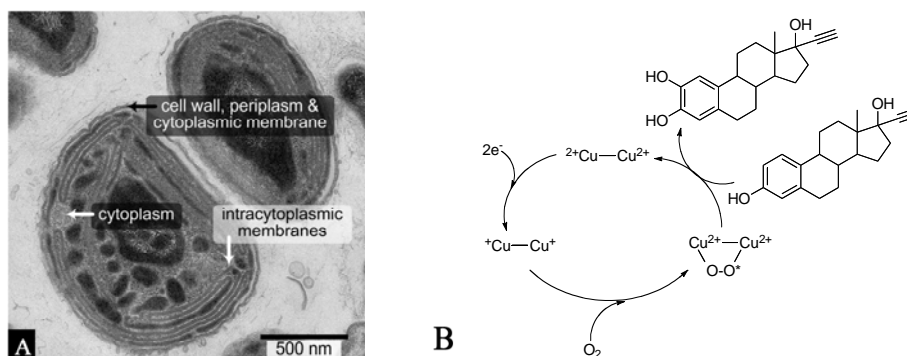


Figure 2 A Transmission electron microscope picture of an AOB-cell with indication of the intracytoplasmic membranes [10], B: Concept of the role of a binuclear copper site in AMO (Yi and Harper, 2007; O-O* is an electrophilic form of oxygen).

A complete biomineralisation occurs in cooperation with the heterotrophic micro-organisms Nitrifying bacteria can oxidize or hydroxylate complex molecules thanks to the non-selective oxidizing enzyme AMO. The intermediates are subsequently used as substrate for the heterotrophic bacteria, present in the nitrifying sludge [11]. Research during the Neptune project showed that heterotrophs isolated from a nitrifying fixed bed reactor (FBR) enhanced the removal of an unidentified metabolite, formed during the co-metabolism of EE2 with NEC. Yet, the isolated heterotrophs were not able to degrade the EE2 molecule itself, indicating the importance of nitrification in the degradation process [6]

The degradation of the natural hormones 17 β -estradiol and estrone, nonylphenol (degradation product of detergents) and bisphenol-A (a component of transparent plastic) is enhanced in nitrifying activated sludge [12; 13]. Also the antibiotic trimethoprim and an X-ray contrast medium iopromide showed better removal in nitrifying sludge [14]. A recent study showed the removal of 10 selected pharmaceuticals (clofibric acid, gemfibrozil, ibuprofen, fenoprofen, ketoprofen, naproxen, diclofenac, indomethacine, propyphenazone and carbamazepine) with a NEC [15]. According to the authors this is due to the diversity of the nitrifiers and the variation in non-specific mono- and dioxygenase enzymes associated with autotrophic nitrifiers and heterotrophs present in symbiosis with the nitrifying community. Nevertheless, the removal of carbamazepine, clofibric acid and propyphenazone was still less than 40% and degradation rates were very low, 0.1 L g_{SS}⁻¹ d⁻¹, which are not sufficient for a post-treatment.

15.3.2 Configuration

The requirement for nitrifiers to enrich and maintain is a high sludge retention time (SRT) of 15-18 days. Several reactor configurations were tested for the NEC post-treatment of secondary effluent. In a MBR, the nitrifier enriched culture (NEC) was able to remove 17 α -ethinylestradiol efficiently at ng L⁻¹ concentrations and with a minimal input of 1 mg NH₄⁺-N L⁻¹ [6]. It was also shown that the level of organic N in WWTP-effluent was sufficient for the nitrification activity to guarantee the co-metabolism of EE2. In a FBR, operating several months without dosage of

ammonium, removal of EE2 was maintained [16]. With NEC in MBR or FBR, it was possible to obtain sufficient EE2 removal at a minimal HRT of 8 h. To enhance the performance of nitrification as a post-treatment of WWTP-effluent it is important to further decrease this HRT.

Estrogen degradation also occurs on a regular post-sandfilter, a more cost-effective technique. Figure 3 shows a regular sand filter, which is enriched with nitrifier washed out from the secondary settler under normal operating conditions. The removal of estrogenic effect observed in a full scale experiment is illustrated in Figure 4.

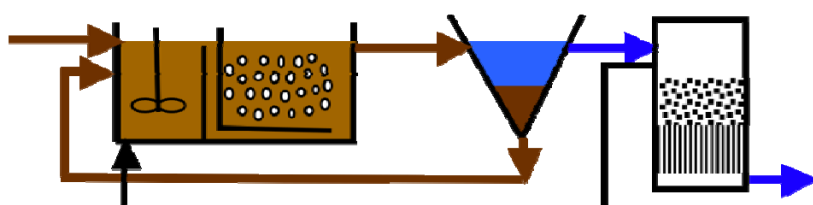


Figure 3 Conventional activated sludge system with denitrification-nitrification, a secondary settler and post-sand filtration enriched with nitrifiers for enhanced estrogen/micropollutant removal).

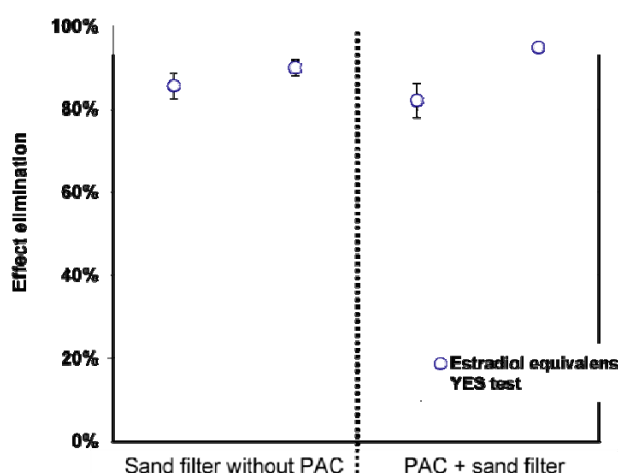


Figure 4 Comparison of the estrogenicity removal achieved by a sandfilter with (right) and without (left) addition of powdered activated carbon (dosing: 15 mg PAC L⁻¹). The experiment was run on a full scale municipal wastewater treatment plant treating 55'000 population equivalents).

15.3.3 Application status

Up till now, only lab-scale reactors have been tested for the removal of EDCs from secondary effluent. In the future, this approach should be tested on a bigger scale and for a broader range of pharmaceuticals. A slow sand filter with NEC as a biofilm on the sand granules could be a new configuration with a lot of potential for the removal of residual estrogenicity from secondary effluent.

The removal of (selected) micropollutants in the aeration tank during nitrification is recently gaining attention and several studies are investigating the relation between nitrification and enhanced micropollutant removal. This is not easy since probably several pathways in nitrifying activated sludge are contributing to the removal of trace compounds. Nevertheless, these studies will be valuable for the optimization of the WWTP for micropollutant removal.

15.4 COSTS

The use of nitrification, a known biological technique, to decrease partly the micropollutant burden on surface waters by removing biological effects such as estrogenicity could be a part of the solution for the trace compounds issue. A sand filter dimensioned for 5 to 7 $\text{m}_{\text{WW}}^3 \text{m}^{-2} \text{h}^{-1}$ has total cost in the range of 0.03 to 0.10 € $\text{m}_{\text{WW}}^{-3}$.

15.5 KNOWLEDGE GAPS

So far, only the co-metabolism of estrogenic compounds during nitrification is clearly shown. To know to what extent the nitrification enzymes are contributing to the removal of other pharmaceuticals, it is necessary to make a distinction between the different pathways. It was already mentioned that high SRT increase the biodiversity of activated sludge and therefore more diverse removal mechanisms occur. Moreover, cooperation by the heterotrophic bacteria seems to occur to further degrade the metabolites of the nitrification co-metabolism. Research of these processes will enhance the knowledge to engineer and optimize the operation of a WWTP.

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16

MICROBIAL FUEL CELLS

16.1 INTRODUCTION

While wastewater treatment was originally focused on nutrient removal, research nowadays focuses on combined solutions for wastewater treatment and energy/resource recovery. Microbial fuel cells (MFC) are a new generation of wastewater treatment that enables direct conversion of the chemical energy of electron donors, such as waste organics, into electrical energy. The main advantage of MFC is the production of electrical energy but without the undesirable formation of excess microbial sludge. It was demonstrated that microorganisms effectively convert glucose (and in extension other organics) to electricity at rates and efficiencies, which are of interest to the environmental technologist [1]. This can occur by means of an enrichment process, leading to a biofilm based reactor with a high and stable performance [2].

Bio-Electrochemical Systems (BES) are based on the same technology but aim for not only partial energy recovery, but also for the valorisation of waste organics through the production of added-value-products. If the net production of power is the objective, the system is referred to as a Microbial Fuel cell (MFC). However, one can also supply electricity to the bacteria to drive particular processes in the cathode compartment. In that case the system is called a Microbial Electrolysis Cell (MEC).

BES can be implemented in a variety of processes for the benefit of the environment. Examples are the oxidation of organics in waters, sediments and the root zone of plants (Figure 1) and the removal of compounds such as organochlorines, nitrates, chlorates and sulfides with concomitant generation of electricity by BES. Moreover, a series of valuable commodities such as methane, hydrogen peroxide, polyhydroxybutyrate and polyphenolics can be produced in a sustainable context by these systems (Table 1).

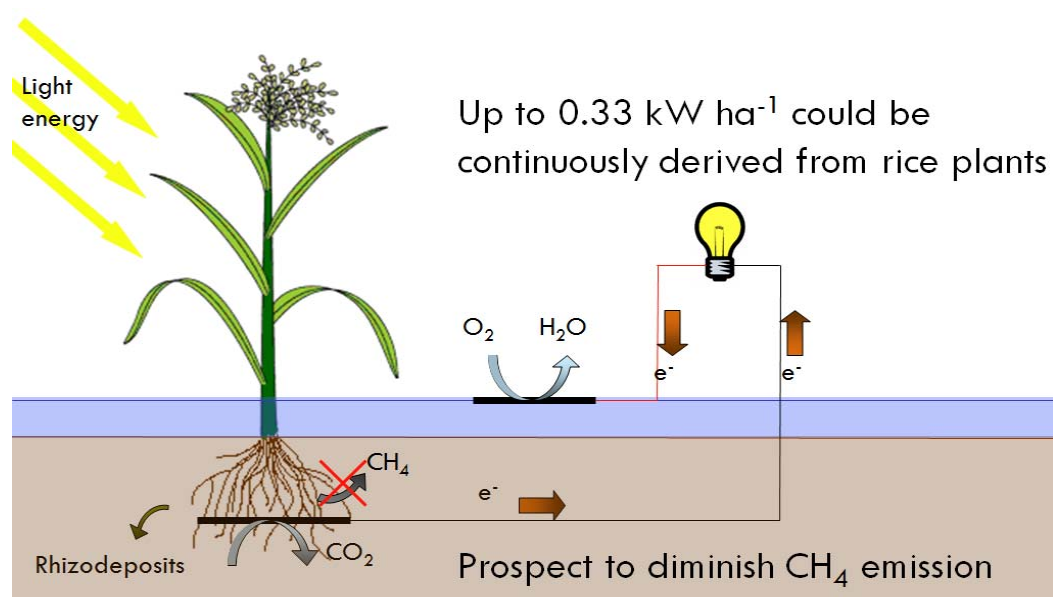


Figure 1 Conceptual view of a BES in association with a sustained plant production

TABLE 1 ENVIRONMENTAL APPLICATIONS OF BES

	Application	Reference
Removal of	Sulfides	[3]
	Nitrates	[4]
	Excess nitrogen in general	[5]
	Perchlorates	[6]
	1,2-dichloroethane	[7]
Production of added-value-products	Methane	[8]
	Hydrogen peroxide	[9]
	Polyhydroxybutyrate	[10]
	Polyphenolics	[10]
	Oxidation of energy rich vegetable products	[11]
	Upgrading anaerobic digestion	[12]
		[13]
	Harvest energy from sediments and from productive plant growing systems	[14]

16.2 SCHEMATIC OUTLINE

BES use biocatalysts for oxidation and/or reduction reactions at electrodes (Figure 2). In this context, the biocatalyst is generally a whole microorganism and the system has two electrodes: an anode and a cathode. BES can oxidize compounds at the anode to generate electrons, which react at the cathode with oxygen or another terminal acceptor. A scheme of a typical reactor is shown in Figure 3.

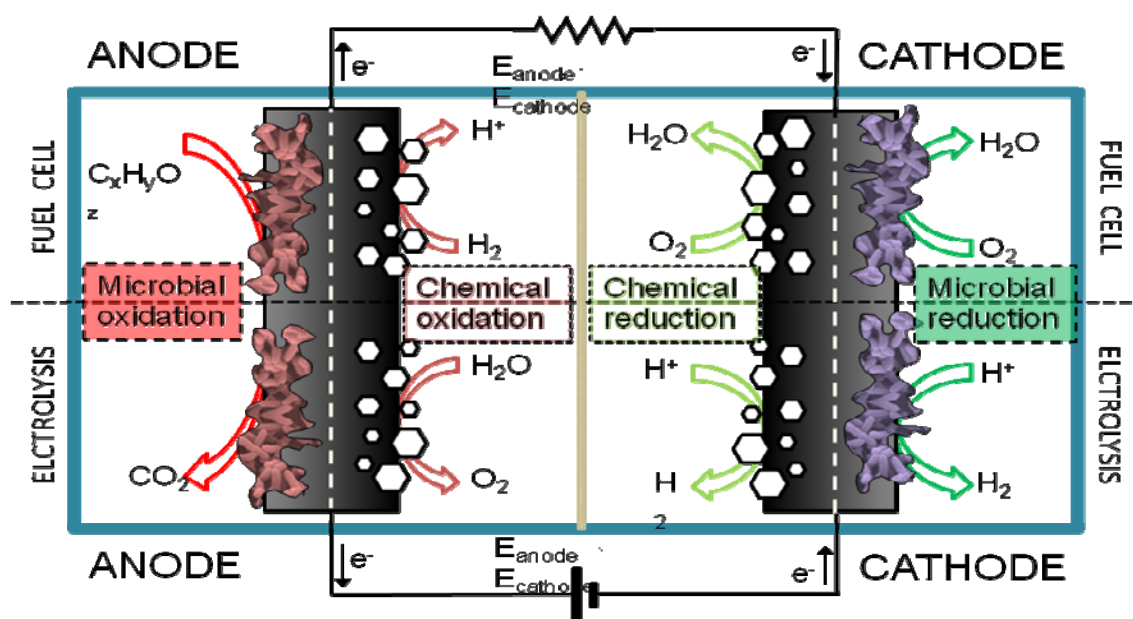


Figure 2 General scheme of the BES either operating to produce electricity or to direct the microbial metabolism by supplying electrical current

In a first application the MFC serves as standalone power source. The MFC is able to deliver power outputs at the desired voltage and current by connecting several MFCs in series or parallel. Several low value but energy rich discrete organic streams can be used as 'fuel' in a MFC, thereby transforming waste into a valuable energy source and decreasing the costs for further treatment. To address the energy recovery of particularly high strength wastewaters, several anaerobic digestion technologies have been developed. Most widespread in this context is the Upflow Anaerobic Sludge Blanket (UASB) reactor, in which methane is produced from industrial wastewater. UASB reactors typically handle highly digestible wastewaters at a loading rate of 10-20 kg COD per m³ reactor per day, and have, with a combustion engine as converter, overall electrical efficiencies of up to 35%, implying a power output of 0.5-1 kW.m⁻³ reactor. However, the digestate i.e. the liquid stream that leaves the anaerobic digester still contains residual levels of volatile fatty acids at a total COD concentration of up to several kg COD m⁻³. By implementing a MFC/MEC (Microbial Electrolysis Cell) unit the residual volatile fatty acids can be converted to electricity and subsequently to hydrogen at a high efficiency [15], [16]. Subsequently, the produced hydrogen can be supplemented to the biogas in order to produce an internal combustion engine fuel (ICE-fuel) with improved quality. The latter can e.g. enable a decrease of the NO_x emissions during combustion. In order to treat low strength wastewaters such as domestic wastewaters, a conventional aerobic wastewater treatment plant (WWTP) is most

commonly used. However, large amounts of excess sludge are produced which can be converted to biogas by means of a conventional anaerobic digester. The digestate still contains residuals of up to several kg COD m⁻³. This digestate can be treated using a MFC, the latter thereby serving as an additional energy recovery technology and polishing step. By retro-fitting the current WWTP and sludge fermentation system, the energy and carbon circle can be further closed.

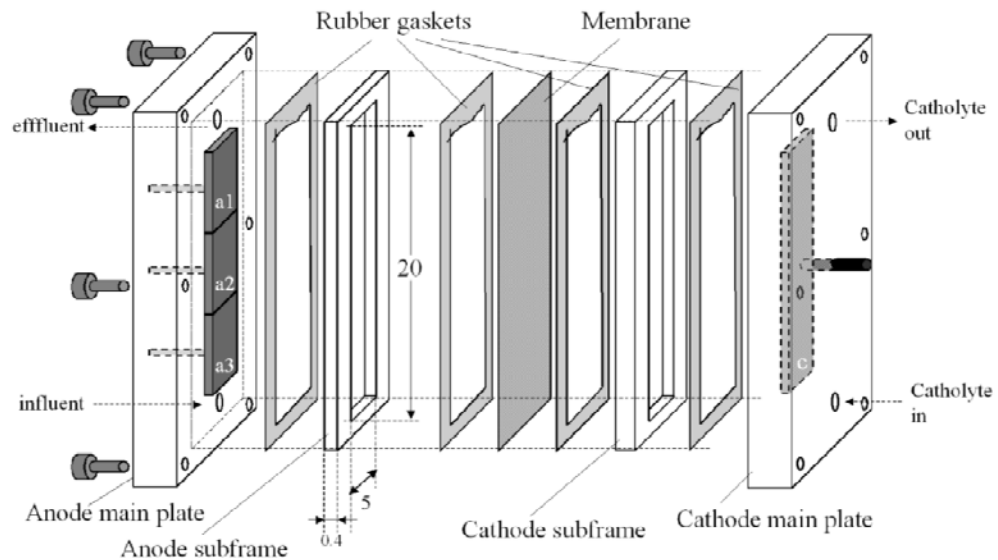


Figure 3 Scheme of a reactor designed to study MFC in the lab. Note: a1, a2, a3: anodic electrode graphite plates (each connected to a graphite rod that is connected with wires to others and to a shared external circuit and data acquisition system); c: cathodic electrode graphite plate (surrounded with graphite granule); Numbers indicate the dimensions (in cm) of the anode working space. [17]

16.3 PROCESS DESCRIPTION

BASIC ASPECTS MICROBIAL ENERGY PRODUCTION

The conversion of substrate into electrical current is catalyzed by microorganisms. In contrast to conventional aerobic and anaerobic wastewater treatment, many basic parameters which are needed to evaluate the microbial performance, are not yet available. The result is Table 2 give an overview of the microbial data reported for MFCs and aerobic and anaerobic processes. Moreover, some typical or 'rule of thumb' values for MFCs are proposed [18].

Table 2 Overview of the parameters describing the microbial processes in MFCs. As a reference, the typical range for both suspended growth and biofilm based aerobic and anaerobic processes are given. Whereas Y: growth yield, X: bioass concentration per volume (v) and surface (f), L_f: biofilm thickness, B_x: sludge loading rate, B_v: volumetric loading rate, E_{KA}: anode half-saturation potential, E_{a,sat}: saturation potential [18].

	MFC Range	MFC Typical value	Aerobic treatment	Anaerobic digestion
Y (gDW.gCOD-1)	0.02-0.23	0.1	0.4	0.05-0.1
XV (kgDW.m-3reactor)	0.25-0.58	0.4	2-4	10-20
Xf (g.m-2)	0.23-1.27	0.25	0.5-1	0.5-1
Lf (μm)	4-64	30	30-200	50-2000
BX (kgCOD.kgDW-1.d-1)	1.51-6.93	3	0.1-0.5	1-2
Bv (kgCOD.m-3reactor.d-1)	0.3-..5	1	0.5-1	10-20
EKA (V vs. Ag/AgCl)	-0.42-(-0.3)	-0.4	n.a.	n.a.
Eq.sat (V vs. Ag/AgCl)	-0.35-0.1	-0.3	n.a.	n.a.

CONFIGURATION

The industrial application is the ultimate goal of MFC technology. To achieve this a continuously working, robust and economically competitive reactor at a cubic meter scale is needed. Several designs, paving the road to scale up, have been proposed and have been successfully tested (Figure 4).

A single chamber microbial fuel cell (SCMFC) containing eight graphite electrodes (anodes) and an internal single air cathode was first reported for the treatment of wastewater [19]. The system was operated under continuous flow conditions with primary clarifier effluent obtained from a local wastewater treatment plant and generated a maximum of 26 mW.m^{-2} while removing up to 80% of the COD of the wastewater. Rabaey et al. [20] developed a tubular reactor system in which the granular anode bed was subsequently circumvented by a membrane and cathode felt. The continuously fed system generated a maximum power output of up to 48 W.m^{-3} MFC. Because the membrane is an effective part of the design, the need for additional construction materials is circumvented. Within the line of tubular shapes, Zuo et al. [21] presented a scalable system suited for retrofitting of existing bioreactors. By the implementation of a tubular membrane cathode assembly together with graphite anode brushes, power could be generated from many rectangular reactors.

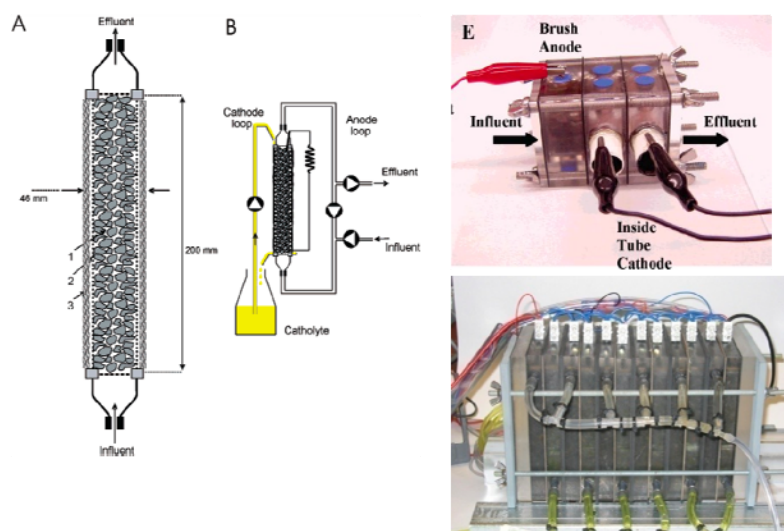


Figure 4 Three designs with scalable features: a tubular design [20], a tubular membrane cathode assembly [21] and a rectangular stacked design [18].

The application of a stacked design, consisting of adjacent frames, as shown in Aelterman [18] boosted the performance by a factor 5 compared to a previously used rectangular design [22]. Li et al. [23] altered the stacked design to the so-called baffled single-chambered design with two groups of electrodes sharing only one anode chamber containing baffles that enable well-mixing of the substrate. This new design with a 10-fold larger electrode area could produce a power output 4-fold higher than that of the normal design.

16.3.1 Application status of BESs

At present, BESs have reached pilot stage testing. In 2007, the Advanced Water Management Centre performed a pilot trial based on the MFC concept, at a brewery in the Brisbane area. The current densities were limited to about 20 A m^{-3} , and it was concluded that conceptually MFCs are complex to operate. Moreover, the value of the generated electrical current is limited. As a follow up development, the AWMC created a BES with as primary objective to produce caustic soda, again at the aforementioned brewery site. This pilot is currently operational, first results obtained were highly promising. In parallel, Penn state university is conducting a pilot trial for a MEC, producing hydrogen, at a winery in California (Napa Valley, CA). It can be expected that BESs will find their way to the market during 2011/2012.

16.4 COSTS

Specific limitations of existing MFC technologies are the cost of materials for the construction of MFCs and their as-yet-low power output in comparison with other bioconversion technologies. The proton exchange membrane (PEM), which is widely used in MFCs, represents a considerable cost (Nafion™ costs approximately \$ 500 per m^2) [24] and increases the internal resistance of the MFC. Attempts were made to replace or remove the PEM but low coulombic

efficiency due to oxygen influx [25] and high internal resistance [26] are still remaining problematic. Overall, major technical hurdles will need to be taken in order to upscale MFC from the present liter scale to the cubic meter scale required for practical application [27]. The technological developments were objectively bench marked to those of competing processes and technical devices [28].

Based on the current densities, power densities and the MFC reactor capital cost (lifetime 10 years), a calculation of the cost for the treatment of wastewater, the cost for the generation of energy and the energy profit per unit of COD treated using MFCs can be made (Table 3). Rozendal et al. [29] estimated that the capital cost for future BESs could be € 0.4 per kg COD. This value is similar to the capital cost based on the future projection scenario. However, based on actual, a decrease of the capital costs by at least a factor 4 are needed [18].

Table 3 Overview of the maximum power densities and corresponding loading rates based on two scenarios (typical estimation and a future projection). The treatment cost and energy production cost are calculated based on a reactor capital cost of € 4.4 per $m^3 \cdot d^{-1}$ and an energy price of € 0.1 per kWh; in addition, the energy profit per kg of COD treated is calculated [18].

Simulation	Power Density		Current Density		Treat cost	Energy cost	Treat. profit
	$W \cdot m^{-3}$	kWh. $m^{-3} \cdot d^{-1}$	$A \cdot m^{-3}$	KgCOD. $m^{-3} \cdot d^{-1}$	€·kgCOD ⁻¹	€·kWh ⁻¹	€·kgCOD ⁻¹
Typical ^a	80	1.9	168	1.2	3.7	2.3	0.16
Projection ^b	800	19.2	1680	12.0	0.4	0.2	0.16

^abased on X_V of 0.4 kg_{VSS}·m⁻³, a B_X of 3 kg_{COD}·kg_{VSS}⁻¹·d⁻¹ and a voltage of 0.47 V

^bbased on X_V of 4 kg_{VSS}·m⁻³, a B_X of 3 kg_{COD}·kg_{VSS}⁻¹·d⁻¹ and a voltage of 0.47 V

16.5 KNOWLEDGE GAPS

In MFC systems, the activity of biocatalysts, electron transfer between bacteria and the anode, internal resistance and overpotentials at both electrodes are the main limiting factors [27].

Electron transfer: The mechanism of bacterial electron transfer to the anodic electrode and the issue of how to improve the electron transfer are still the focus of much controversy. Which mechanisms that electroactive bacteria employed in their electron transfer processes should be clarified. Based on that, good approaches could be established to improve the performance of MFCs upon improving the electron transfer.

Internal resistance: This is a common problem that MFC designers face. A high internal resistance causes a considerable potential

drop due to ohmic losses (Figure 5) [30]. With or without the proton exchange membrane, the internal resistance still remains a limiting factor [26]; [25]. This aspect is one of the crucial bottlenecks hampering upscale of the present technology. Upon increasing the MFC size, the internal resistance will at best remain at the same level, while the current flowing through the system increases and causes considerable potential losses. As such, the size of the upscaled MFC will be limited.

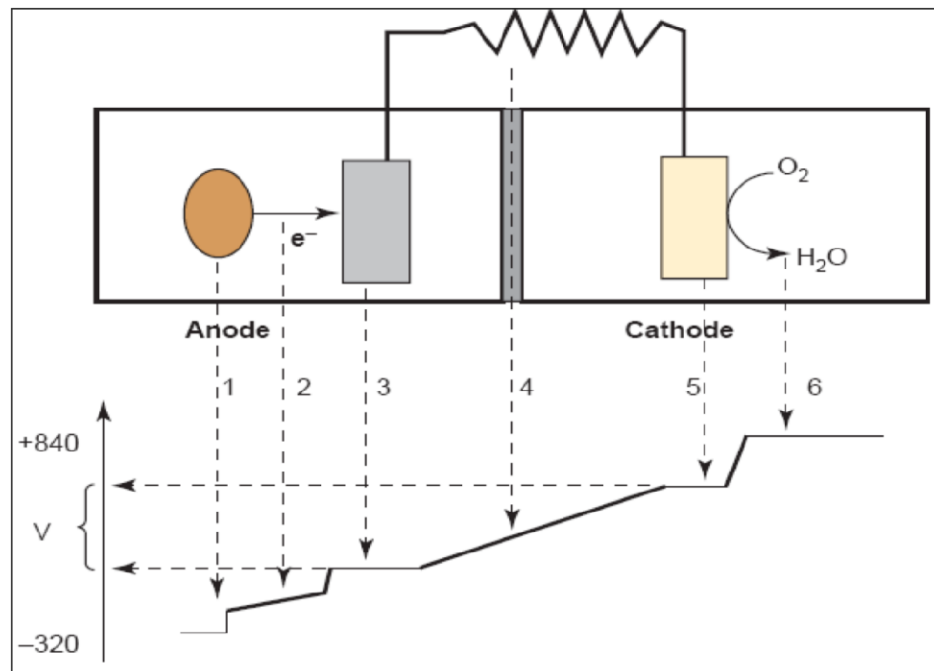


Figure 5 Potential losses during electron transfer in a MFC, after Rabaey and Verstraete [31]. 1. Loss owing to bacterial electron transfer; 2. Losses owing to electrolyte resistance; 3. Losses at the anode; 4. Losses at the MFC resistance (useful potential difference) and membrane resistance losses; 5. Losses at the cathode; 6. Losses owing to electron acceptor reduction.

The activity of biocatalysts: The microbial communities and the microbial activity in MFCs are not well understood. Some research elucidates that biofilms are a common structure of microbial communities in MFCs [32]; [33]; [20] and that facultative anaerobes are usually present in electrochemically active consortia [33]; [34]; [2]. In the last years and during the Neptune project, substantial efforts have been performed to understand the complex community of bacteria in the anode compartment [35]. With the development of the bio-cathode, also the cathodic community was investigated [36].

Cathode reaction: The cathode reaction is considered as one of the key factors limiting the performance of an MFC [37]; [34]; [38]. In many MFC systems, oxygen is the cathodic electron acceptor but usually the poor contact between gaseous oxygen and the cathode, and the imperfect catalysis of the reaction limits the turnover rate. In addition, oxygen leaking to the anode can occur in such systems reducing electricity generation efficiency. The leaking should not be significant, yet still providing high rate electrode reactions. Moreover, to overcome this limitation, platinum has been used as the catalyst [37]; [34] and gas diffusion layers were installed. However, the disadvantage of platinum is that it is not only expensive but it also suffers from sulphide diffusion through the proton exchange membrane

towards the cathode, which poisons the catalyst. Oxygen is still the only good final oxidant candidate to ensure the sustainability of MFCs. In order to improve the cathode-oxygen contact, the use of some electro-catalytic metals in integration with carbon as the electrode material for 'open-air' cathodes is now a promising approach for the improvement of cathode reaction [39]; [40]. Recently biologically catalysed open air cathodes with autotrophic microorganisms that have the catalytic activity comparable to platinum has been developed [36]; [41]. This can be considered as a significant achievement as the microbial catalysts at the cathode allows a decreased material cost and a completely sustainable and environment-benign performance of MFCs. However, limitations still lie in the interaction between the cathode electrode and the microbial catalysts.

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