New wastewater treatment concepts towards energy saving and resource recovery

Rungnapha Khiewwijit

Thesis committee

Promotor

Prof. Dr H.H.M. Rijnaarts
Professor of Environmental Technology
Wageningen University

Co-promotors

Dr K.J. Keesman
Associate professor, Biobased Chemistry and Technology Group
Wageningen University

Dr B.G. Temmink
Assistant professor, Sub-department of Environmental Technology
Wageningen University

Other members

Prof. Dr A.J.M. Stams, Wageningen University
Prof. Dr C. Kroeze, Wageningen University
Prof. Dr I. Nopens, Ghent University, Belgium
Dr P. van der Steen, UNESCO-IHE, Delft

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New wastewater treatment concepts towards energy saving and resource recovery

Rungnapha Khiewwijit

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For my beloved family

Contents

Chapter 1

General introduction

1.1 Conventional wastewater treatment

Conventional activated sludge (CAS) systems are widely applied to treat municipal wastewater. The key processes here are aerobic oxidation of organic pollutants, biological nitrogen (N) removal and chemical or biological phosphorus (P) removal. The main advantages of CAS systems are that they are robust and generally produce an effluent quality that meets the discharge guidelines. However, CAS systems cannot be considered sustainable because they consume large amounts of energy (mainly for aeration), have a high CO_2 emission and do no recover valuable resources such as N and P. In addition, CAS systems produce and have to dispose of large amounts of primary sludge (PS) and excess activated sludge (AS).

More recently, municipal wastewater has started to be considered for its potential resources. For example, the organic pollutants in municipal wastewater represent a potential chemical energy of 1.5–1.9 kWh per m^3 of wastewater, which is more than twice the energy consumption of CAS systems (McCarty et al., 2011). Unfortunately, in CAS systems the largest portion of the energy stored in organics is destroyed by aerobic mineralization to CO_2, and only less than 20% of the municipal wastewater organic matter is recovered as energy-rich methane gas by digesting the PS and AS (Cao, 2011). In CAS systems treating municipal wastewater, large amounts of the valuable nutrients are not recovered since N is emitted as N_2 and P is wasted with the excess sludge. Thus, new ways of wastewater treatment need to be considered to recover more energy and nutrients, and when sufficiently treated the relatively clean water can be reused, for example as irrigation water or industrial process water (Akanyeti et al., 2010; DOW, 2013).

1.2 New developments in municipal wastewater treatment

The activated sludge process was first developed in the early 1900s and today is the most popular treatment process for municipal wastewater (Orhon, 2014). Recovery of energy and nutrients from municipal wastewater is gaining a lot of attention worldwide, and this asks for new combined treatment and recovery concepts (Boelee et al., 2012; Desmidt et al., 2015; Remy et al., 2014; Roeleveld et al., 2010; Sheik et al., 2014; Verstraete et al., 2009). However, the feasibility of such concepts is strongly influenced by wastewater composition and location.

Municipal wastewater is diluted with respect to the concentration of valuable compounds and generally has a low temperature, in particular in temperate and cold climate regions (Metcalf and Eddy, 2004). Both of these aspects make implementation of recovery concepts more difficult. Still, such concepts need to be developed and implemented because apart from the recovery of valuable resources they also would save considerable amounts of energy and chemicals used today by CAS systems.

1.2.1 Organic matter

Anaerobic digestion of organic matter to methane is commonly used for efficient energy recovery from municipal wastewater (Metcalf and Eddy, 2004), although only from the more concentrated PS and AS streams, and at relatively high temperatures (typically 35°C). Low temperature anaerobic digestion of all municipal wastewater organics has been investigated by several studies (Mahmoud et al., 2004; Zhang et al., 2013; Zhang et al., 2012). They combined a low temperature (15°C) upflow anaerobic sludge blanket (UASB) reactor, to convert soluble biodegradable COD (chemical oxygen demand) into methane, with a mesophilic anaerobic digester (35°C) to produce methane from wastewater suspended organic solids. They showed that this combined process is technologically feasible, but still needs further optimization.

More efficient recovery of organic matter, either as energy or as chemicals such as volatile fatty acids (VFA) (see Section 1.3) (Lee et al., 2014), requires a pre-concentration step. Examples of pre-concentration methods are direct membrane filtration, dissolved air flotation and flocculation with inorganic metal salts or synthetic polymer (Verstraete et al., 2009). However, all of these methods require a large input of energy and/or chemicals. The main technological challenge therefore is to develop a pre-concentration method that combines a high recovery efficiency with a low energy consumption.

Bioflocculation with HL-MBR to concentrate organic matter

An integrated aerobic bioflocculation process and direct membrane filtration is a promising pre-concentration method for municipal wastewater organic matter (Akanyeti et al., 2010; Faust et al., 2014a; Faust et al., 2014b). Bioflocculation is an aerobic biological process in which colloidal and suspended COD are flocculated with the aid of extracellular polymeric substances

(EPS) produced by microorganisms (Faust, 2014). Bioflocculation has been successfully conducted in a high-loaded membrane bioreactor (HL-MBR), which operates under extremely short hydraulic retention time (HRT) of 0.7–1.2 hours and sludge retention time (SRT) of 0.5–1 days (Akanyeti et al., 2010; Faust et al., 2014b). The short SRT guarantees that mineralization of COD to CO_2 is largely avoided. The short HRT results in a high concentration of organic matter. Akanyeti et al. (2010) reported a methane yield of 35% of sewage COD by bioflocculation in an HL-MBR, which is almost two times the recovery when anaerobic digestion is applied on PS and AS generated by CAS systems (Cao, 2011). An additional advantage is that the HL-MBR permeate can be used for irrigation because it contains high amounts of N and P, and is free of solids and pathogens.

1.2.2 Nitrogen

CAS systems remove N by subsequent biological nitrification and denitrification. Nitrification is the process by which ammonium is sequentially oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-) by two groups of autotrophic nitrifying bacteria, i.e. ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). During denitrification nitrate is reduced to dinitrogen (N_2) gas. This is a heterotrophic process, i.e. it requires organic carbon. Recovery of N is less urgent than recovery of P, which is a finite resource and expected to become a scarce resource in the near future (Cordell et al., 2011). Still, recovery of N from municipal wastewater could save a lot of energy otherwise needed to produce N fertilizers with the Haber-Bosch process (Maurer et al., 2003). Although several physical-chemical N recovery technologies are available, for example stripping and thermal evaporation, these would not be economical feasible at typical municipal wastewater concentrations of 20–70 mg N/L (Metcalf and Eddy, 2004; Mulder, 2003; Wilsenach et al., 2003). Thus, the focus should be on new biological N removal technologies, such as partial nitritation combined with Anammox (anaerobic ammonium oxidation) that are more energy efficient than a conventional nitrification/denitrification and do not consume valuable organic carbon sources (Fux and Siegrist, 2004).

<u>*Partial nitritation and Anammox*</u>

Combined partial nitritation and Anammox is already applied on full-scale to treat digester effluent, which have high temperatures (>30°C) and contain high concentrations of ammonium (>700 mg N/L) (van der Star et al., 2007). There are several advantages of this concept over the conventional nitrification/denitrification: (1) less energy consumption for aeration, (2) reduced CO_2 emission and (3) a lower sludge production (Fux and Siegrist, 2004). The application of combined partial nitritation and Anammox process down to very low temperatures (10°C) and at low ammonium concentrations has been explored by several studies (Gilbert et al., 2015; Hendrickx et al., 2014; Hendrickx et al., 2012). The study of Hendrickx et al. (2014) showed that the Anammox process is feasible at a temperature of 10°C and a diluted stream of approximately 60 mg N/L. However, the main bottleneck may be the partial nitritation operated at low temperatures (Hao et al., 2002; Kim et al., 2008).

1.2.3 Phosphorus

As was mentioned earlier, phosphorus is a non-renewable resource and becomes progressively limited. Using Dutch municipal wastewater as an example, if all the P available in municipal wastewater would be recovered, this is equivalent to more than 50% of the Dutch artificial P fertilizer consumption (de Graaff, 2010). This is the motivation to develop novel P recovery technologies. Examples of phosphate recovery technologies from wastewater streams and wastewater sludge are presented in Table 1.1.

Unfortunately, most of the technologies presented in Table 1.1 have a high energy and/or chemical demand. In addition, most of them only work effectively if the concentration of P is relatively high, such as in digester liquors or in urine. Therefore, the main challenge is to develop cost effective technologies that can also recover P from more diluted wastewater streams, such as municipal wastewater with typical concentrations of 5–15 mg P/L (Metcalf and Eddy, 2004). It is expected that such a technology will become available in the near future (Desmidt et al., 2015). Therefore, in the present study cost-effective P recovery technology was not further substantiated but was assumed to be already available.

Table 1.1: Examples of phosphate recovery processes for wastewater streams and wastewater sludge

Recovery technology/process	Recovery product	Reference
1. Chemical phosphorus precipitation with iron, calcium, aluminum and magnesium	Iron phosphate Calcium phosphate Aluminum phosphate Struvite	de-Bashan and Bashan (2004)
2. Electrochemical phosphate recovery	Calcium phosphate	Kappel et al. (2013)
3. Reversible adsorption on iron oxides	Concentrated phosphorus	Martin et al. (2009)
4. Thermochemical of sewage sludge ashes	Phosphate-fertilizer	Adam et al. (2009)
5. Phospaq® struvite reactor	Struvite	Driessen et al. (2009)
6. Calcium phosphate Crystalactor®	Calcium phosphate	Wilsenach and Loosdrecht (2002)
7. Chemical phosphorus precipitation after anaerobic digestion of EBPR[a] sludge	Calcium phosphate and struvite	Yuan et al. (2012)
8. Novel membrane separation	Concentrated phosphorus	Hong et al. (2009)

[a] EBPR = Enhanced biological phosphorus removal

1.2.4 New technologies

Several technologies have been recently developed for municipal wastewater treatment, such as microalgae treatment, which is already applied in practice but not to recover N and P, Nereda® technology and several bioelectrochemical technologies, and discussed below.

Microalgae treatment

Microalgae for treating municipal wastewater can be applied in different configurations as described by Boelee et al. (2012). Microalgae systems for municipal wastewater treatment are a promising candidate because of a valuable biomass production, and a reduction of aeration energy otherwise needed to remove N by conventional nitrification/denitrification or partial nitritation/Anammox. However, irradiance and temperature conditions have a significant effect on the microalgal biomass productivity (Boelee et al., 2014; Slegers et al., 2011) and therefore the specific location determines the applicability.

Nereda® technology

A new wastewater treatment technology based on aerobic granular sludge was introduced in 2003 and is also known as the Nereda process (van der Roest et al., 2011). Nereda has advantages over traditional CAS systems, i.e. a reduction in energy consumption and a smaller footprint (Giesen et al., 2013). However, similar to CAS systems with Nereda most of the organic matter is aerobically mineralized and neither N nor P are recovered.

Bioelectrochemical systems

Bioelectrochemical cells have been developed to produce electricity from wastewater and even to recover N from concentrated streams such as urine (Arredondo et al., 2015; Heijne et al., 2010; Kuntke et al., 2012). Although these bioelectrochemical systems look promising, their application so far has been limited to artificial wastewaters and/or small scales.

1.3 Volatile fatty acids (VFA) production

In CAS systems energy recovery from wastewater is accomplished by anaerobic digestion of the (organic) solids in PS and AS into methane. As mentioned earlier, VFA may be preferred over methane. Figure 1.1 gives an overview of the four steps during anaerobic digestion. It also shows potential applications of VFA, which are intermediate digestion products.

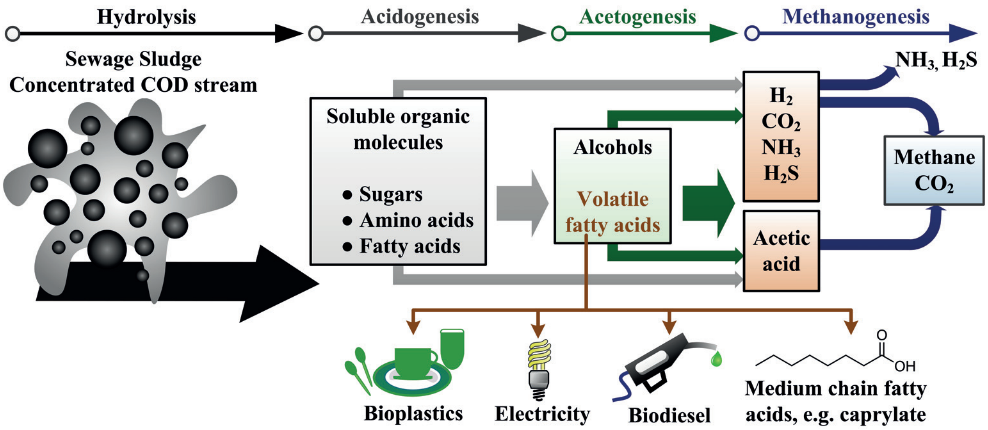

Figure 1.1: Anaerobic digestion process and potential applications of volatile fatty acids with examples of possible productions from VFA

These VFA mainly consist of short-chain fatty acids with two to five carbon atoms: acetate (C2), propionate (C3), butyrate (C4), and valerate (C5). Production of VFA can be used as the starting compounds for a wide range of valuable products, for example medium-chain fatty acids, electricity, bioplastics (polyhydroxyalkanoate or PHA), and biodiesel (Lee et al., 2014). However, VFA production is only possible if the last step, i.e. methanogenesis, can be prevented. This can be accomplished by applying a short SRT to actively wash-out the slow growing methanogens and/or by applying extreme pH values that inhibit growth of methanogens (Chen et al., 2007). Many studies have demonstrated that anaerobic fermentation of PS and AS at high pH values can significantly enhance solids degradation and promote wash-out of methanogens, and in this manner gives a higher VFA yield compared to acidic or neutral pH conditions (Chen et al., 2007; Jie et al., 2014; Liu et al., 2012; Maspolim et al., 2015; Zhang et al., 2009). However, to achieve a maximum organic matter recovery and make high pH VFA fermentation an economically feasible technology for municipal wastewater treatment, first a pre-concentration step, i.e. bioflocculation in an HL-MBR, needs to be applied.

1.4 Modelling process networks for design and control wastewater treatment

Mathematical models are useful tools to evaluate the responses to changes in system operations or influent loads. Availability of input and output data determines the type of mathematical model, which is often divided into white-box (mechanistic), black-box (phenomenological) models, or a combination of these, which are known as grey-box (semi-physical) model (Carstensen et al., 1997). A white-box model solely follows from prior physical knowledge of the system. Although white-box model leads to more accurate evaluation results than black-box model under changing conditions, it is usually more complex and requires more computational effort. A black-box model is relatively simple, but the results are only valid under the experimental conditions. Therefore, a semi-physical model can take advantage of both approaches: all insight about the process or system is reflected in the white-box part, but the missing information is represented by empirical (black-box) relationships using the available experimental data (Romijn et al., 2008).

In addition to the information availability, mathematical models can be developed using either a static or dynamic approach. A static or steady-state approach gives time-independent results, whereas dynamic results are able to show predictions as a function of time. Dynamic models describe the wastewater treatment process can be found in the literature, for example the benchmark simulation model (BSM) and anaerobic digestion model (ADM) (Alex et al., 2008; Jeppsson et al., 2007; Rosen et al., 2006).

In the current study, a steady-state semi-physical modelling approach, using an Excel-based model, is used to simulate and combine individual process units into a plant-wide simulation. A number of studies have investigated on modelling of the individual process, but not much research has been conducted towards integrated or plant-wide modelling. Examples of plant-wide modelling for wastewater treatment are found in the studies of Nopens et al. (2009) and Rosen et al. (2006). In this thesis quantitative scenario-based calculations are based on mass and energy balances with simple conversion relationships and on existing experimental data, while neglecting the storage term in each process unit. Similar approach has also been applied in other studies for wastewater treatment (Boelee et al., 2012; Garrido et al., 2013; Tervahauta et al., 2013; Tsuzuki et al., 2013).

1.5 Outline of this thesis

The objective of this thesis was to explore the feasibility of new municipal wastewater treatment concepts that help to improve energy saving and resource recovery by modelling and experiments. Special focus of the experiments was set on the recovery of organic matter in the form of VFA production. Figure 1.2 provides an overview of the research that was carried out to accomplish this.

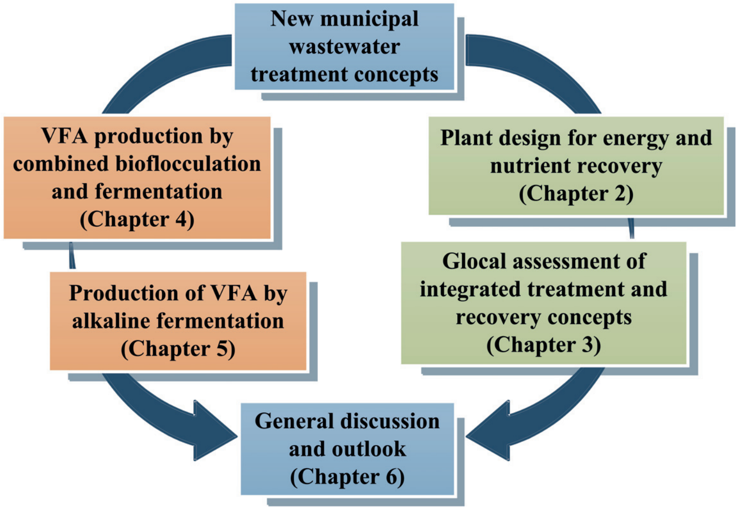

Figure 1.2: Overview of the research that was carried out to investigate new municipal wastewater treatment concepts. Green box indicates modelling work and orange box indicates experimental work.

Chapter 2 of this thesis describes a procedure to design and integrate new process units into wastewater treatment plant configurations with promising perspectives for resource recovery. A numerical simulation tool using an Excel-based model was developed based on literature data and on information from laboratory scale experiments. Two configurations were selected from 11 initial configurations and were further explored using the Netherlands as a case study. Their performance was evaluated by several key performance indicators (KPIs). Also, a "one-at-a-time" sensitivity and global sensitivity analyses were conducted to investigate the effect of temperature and wastewater composition on energy consumption, energy production and net energy yield.

In **Chapter 3** the feasibility of the two configurations suggested in Chapter 2 was further evaluated under different locations around the globe, as we name here a glocal assessment analysis. Quantitative numerical results based on the KPIs and area requirements for microalgae cultivation, in terms of light intensity and temperature, were compared. A sensitivity analysis on the microalgal biomass yield, microalgal maintenance coefficient and wastewater composition was investigated for a microalgae treatment with respect to area requirement and effluent quality.

In **Chapter 4** the technological feasibility of combined bioflocculation to concentrate sewage organic matter, using an HL-MBR, and anaerobic fermentation to produce VFA was experimentally investigated. The sewage COD, N, and P mass balances in bioflocculation and anaerobic fermentation were discussed and compared with CAS systems.

In **Chapter 5** a novel approach to enhance VFA production from sewage by combined aerobic bioflocculation and alkaline sequencing batch fermentation was investigated. Solids degradation, VFA production and VFA composition were compared to a fermentation process without pH control. In addition, a constant high pH control was compared to a short-term high pH shock in an attempt to even further increase VFA production from sewage.

In **Chapter 6** three novel municipal wastewater treatment plant configurations, based on bioflocculation, anaerobic fermentation, partial nitritation/Anammox and microalgae treatment that allow recovery of valuable resources and improve energy saving, are proposed. Based on the main findings from experimental work the overall sustainability in terms of energy saving and potential for sewage organic matter recovery from bioflocculation and alkaline anaerobic fermentation are further discussed and compared with CAS systems. This chapter also presents an outlook and recommendations for further research, in particular to make VFA production economically more attractive.

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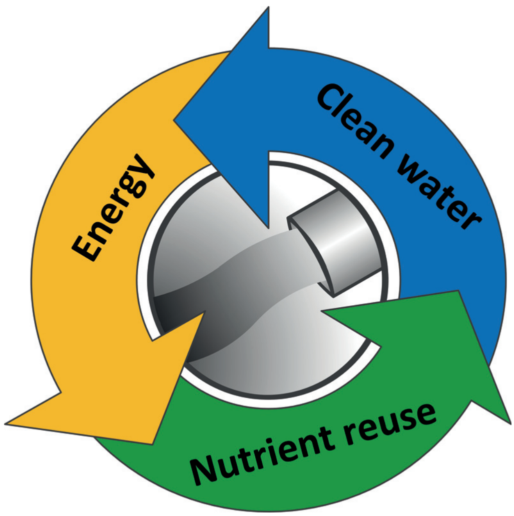
Chapter 2

Energy and nutrient recovery for municipal wastewater treatment: How to design a feasible plant layout?



Abstract

Activated sludge systems are commonly used for robust and efficient treatment of municipal wastewater. However, these systems cannot achieve their maximum potential to recover valuable resources from wastewater. This study demonstrates a procedure to design a feasible novel configuration for maximizing energy and nutrient recovery. A simulation model was developed based on literature data and recent experimental research using steady-state energy and mass balances with conversions. The analysis showed that in the Netherlands, proposed configuration consists of four technologies: bioflocculation, cold partial nitritation/Anammox, P recovery, and anaerobic digestion. Results indicate the possibility to increase net energy yield up to 0.24 kWh/m^3 of wastewater, while reducing carbon emission by 35%. Moreover, sensitivity analysis points out the dominant influence of wastewater organic matter on energy production and consumption. This study provides a good starting point for the design of promising layouts that will improve sustainability of municipal wastewater management in the future.

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2.1 Introduction

Biological treatment of municipal wastewaters is mostly accomplished in conventional activated sludge (CAS) systems. This also holds for municipal wastewater treatment in the Netherlands (Stowa, 2010). A CAS system is designed to produce an effluent that meets the discharge guidelines by removing organic pollutants and the nutrients, nitrogen (N) and phosphorus (P). Although CAS systems are very robust, they cannot be considered sustainable. A major drawback is the high energy consumption, mainly for aeration which accounts for about half of the total energy consumption of 0.6 kWh per m^3 of wastewater (McCarty et al., 2011). Municipal wastewaters with typical organic matter concentrations (expressed in chemical oxygen demand or COD) of 400–500 mg COD/L (Owen, 1982) contain a potential chemical energy of 1.5–1.9 kWh per m^3 of wastewater, which is more than twice the energy demand of a typical CAS system. In CAS systems this energy is largely destroyed by aerobic mineralization of the sewage organic matter to CO_2. Another drawback is that no N and P, and only a limited amount of energy contained in the organic pollutants, are recovered. The commonly used processes for nutrient removal are biological nitrification/denitrification for N-removal and chemical or biological P-removal. These processes result in a loss of N and P. In particular P that comes from mines and can become scarce in the future, whereas N_2 is abundantly available in the atmosphere (de Ridder et al., 2012; Schröder et al., 2010). Therefore, P in municipal wastewater is considered a valuable source for possible reuse as a fertilizer. For example, de Graaff (2010) reported that the total amount of P that can be found in Dutch municipal wastewater corresponds to more than 50% of the artificial P fertilizer used in the country.

Several novel sustainable wastewater treatment and resources recovery technologies are available; however, little is known about how to integrate such technologies in municipal wastewater treatment plants (WWTPs). Therefore, a simulation approach could be an appropriate tool to develop new configurations for future municipal WWTPs and to predict the feasibility of these configurations. Such an approach has already been used for different applications, for example, for separation at source configurations in which urine and black water are separately treated (Tervahauta et al., 2013; Wilsenach and van Loosdrecht, 2006), for wastewater treatment configurations based on microalgae biofilms (Boelee et al., 2012), for optimizing the urban water infrastructure systems (Agudelo-Vera et al., 2012; Hiessl et al., 2001), for development of a benchmarking methodology for advanced control in oxidation ditch municipal WWTPs (Abusam, 2001), and for identifying the future potential energy contribution from wastewater (Heubeck et al., 2011). However, limited information can be found in the literature on integration of both treatment and resource recovery perspectives on the future of municipal WWTPs, whereas municipal wastewater can be considered as a valuable source of water and nutrients in agriculture (Verstraete et al., 2009). Also, knowledge-based decision support systems (DSSs) and life cycle assessment (LCA) methods are used to facilitate an appropriate or optimal WWTP design with different objectives and requirements. However, so far these are limited to conventional wastewater treatment systems and the results are largely dependent on the data quality and their specifications (Aulinas et al., 2011; Garrido-Baserba et al., 2014; Rivas et al., 2008; Wang et al., 2012).

The objective of this study is to introduce and demonstrate a quantitative procedure to analyze future municipal WWTPs that minimize energy input and CO_2 emission, maximize energy production and recovery of valuable nutrients, and meet the effluent discharge guidelines. The Excel-based simulation tool presented in this study allows investigation of the feasibility of novel configurations for municipal wastewater treatment. For this purpose these configurations are compared to a reference CAS system based on several performance indicators related to conditions in the Netherlands/Western Europe. Additionally, a sensitivity analysis is performed for temperature and wastewater characteristics to extrapolate the results to other countries and climate regions.

2.2 Materials and Methods

An Excel-based model was developed, based on literature data and on information from laboratory scale experiments with selected wastewater treatment and recovery processes. In this study, to compare new configurations with the reference CAS system, the model was constructed from available removal, and recovery efficiencies under steady-state conditions. As our focus is on design, and not monitoring and control, kinetics and time variations were not yet part of this study.

2.2.1 Potential integrated treatment processes

Potential sustainable wastewater treatment and recover processes considered in this study were: i) the subsequent bioflocculation, anaerobic digestion, and combined heat and power (CHP), ii) cold partial nitritation/Anammox, iii) P recovery technology, and iv) microalgae systems with the removal of COD. In this study P recovery is expressed in terms of an assumed recovery efficiency. For an overview of P recovery technologies, we refer to de-Bashan and Bashan (2004).

2.2.1.1 Bioflocculation, anaerobic sludge digestion and CHP

Bioflocculation is a possible technique to concentrate sewage organic matter, similar to the A-stage in an AB process design (Boehnke et al., 1997). Aerobic microorganisms produce extracellular polymer substances (EPS) that facilitate the flocculation between the microorganisms and sewage organic matter (Salehizadeh and Shojaosadati, 2001). Bioflocculation of municipal wastewater results in a concentrated stream of sewage organic matter, from which methane can be produced by anaerobic sludge digestion (Akanyeti et al., 2010). To separate the organic sludge from the effluent, a settler or a membrane can be used. In this study, a settler is chosen due to its simplicity with low operational and maintenance cost. In addition, the underflow of the settler is further dewatered using a thickener to achieve the desired concentration of bioflocculation concentrate before digestion. Subsequently, a CHP unit is used to produce energy and heat from the methane formed in the anaerobic digestion. The removal and conversion efficiencies and design specifications of the integrated bioflocculation, anaerobic digestion and CHP process are presented in Table 2.1.

Table 2.1: Efficiency, conversion and design parameter values for bioflocculation, anaerobic sludge digestion, and CHP process

Process	Unit	Value used	Reference
Bioflocculation			
• Total COD removal efficiency[e]	%CODtotal	80	Akanyeti et al. (2010)
• COD substrate need for biomass growth	% CODbs[d]	40	Design parameter
• O_2 need	g O_2/g $CODbs_{removed}$	0.51[a]	–
• CO_2 production	g CO_2/g $CODbs_{removed}$	0.70[a]	–
• Biomass yield	g VSS/g $CODbs_{removed}$	0.40	Metcalf and Eddy (2004)
• COD in biomass	g COD/g VSS[d]	1.42	Metcalf and Eddy (2004)
• N in biomass	g N/g VSS	0.124	Metcalf and Eddy (2004)
• P in biomass	g P/g VSS	0.027	Metcalf and Eddy (2004)
• Thickener capacity	g COD/L	50	Design parameter
Anaerobic sludge digestion			
• Total COD removal efficiency	% CODb[d]	70	Cakir and Stenstrom (2007)
• Methane production	g CH_4/g $COD_{removed}$	0.23[b]	–
• CO_2 production	g CO_2/g $COD_{removed}$	0.64[b]	–
• Biomass yield	g VSS/g $COD_{removed}$	0.058[b]	Metcalf and Eddy (2004)
• COD, N, P in biomass (see bioflocculation)			
CHP			
• Electricity recovery	%	38	Verstraete and Vlaeminck (2011)
• Heat recovery	%	40	Verstraete and Vlaeminck (2011)
• Energy loss	%	22	–
• CO_2 production	g CO_2/g CH_4[d]	2.75[c]	–
• Enthalpy of combustion	kWh/kg CH_4	13.9	H2moves.eu (2006)

[a] Assuming acetate as organic matter (1.07 g COD/g acetate), the following stoichiometric equation is used for aerobic, heterotrophic oxidation of organic matter (Metcalf and Eddy, 2004): $5CH_3COO^- + NH_4^+ + 5O_2 \rightarrow C_5H_7O_2N + 4H_2O + 5CO_2 + 4OH^-$.

[b] Assuming acetate as COD the following stoichiometric equation is used for anaerobic digestion (Gavala et al., 2003): $CH_3COO^- + 0.032NH_4^+ + 0.968H^+ \rightarrow 0.92CH_4 + 0.92CO_2 + 0.032C_5H_7O_2N + 0.096H_2O$.

[c] The following stoichiometric reaction is used for converting methane to heat and power (Wett et al., 2007): $0.5CH_4 + O_2 \rightarrow 0.5CO_2 + H_2O$ + heat + energy.

[d] Chemical oxygen demand (COD), biodegradable COD (CODb), biodegradable soluble COD (CODbs), methane (CH_4), and biomass expressed in volatile suspended solids (VSS).

[e] Data from lab-scale high-loaded membrane bioreactor conducted at temperature 20°C (Akanyeti et al., 2010).

2.2.1.2 Cold partial nitritation/Anammox

Partial nitritation/Anammox process is a more sustainable process than subsequent nitrification and denitrification processes applied in CAS systems. In the partial nitritation stage, ammonium is partly nitrified to nitrite (Giusti et al., 2011). In the Anammox stage, the produced nitrite is subsequently denitrified in combination with the residual ammonium to form dinitrogen (N_2) gas and nitrate (Cui, 2012). It is important to note that about half of the ammonium should convert into nitrite during the partial nitritation, so that the nitrite-to-ammonium ratio in the effluent will be about 1.3:1 as required for Anammox process. This optimal ratio can be obtained by control of the sludge retention time (SRT), alkalinity, and/or oxygen concentration. Some research models have used an alkalinity/ammonium ratio around 1 with the SRT between 1 and 2.5 days as favorable conditions for the partial nitritation/Anammox process and a dissolved oxygen concentration around 1 mg O_2/L considered as suitable value for the partial nitritation step (Zhang et al., 2008).

One main advantage of the partial nitritation/Anammox process is a lower aeration need compared to the nitrification/denitrification process, as only part of the ammonium is nitrified. Since ammonium is not completely converted into nitrate but only to nitrite, a 50–60% savings on oxygen consumption can be achieved in comparison to full nitrification usually applied in CAS systems. Because Anammox is an autotrophic denitrification process, valuable carbon sources in the sewage can be retained for methane production or other end-products and the addition of external carbon sources are no longer required. The overall estimated cost for a full-scale plant (2.5 €/kg $N_{removed}$) is lower than that for a plant using nitrification/denitrification (3–4 €/kg $N_{removed}$) (Fux and Siegrist, 2004). This cost reduction is due to decreases in biomass production yield, aeration energy, and additional chemical inputs. Although not yet applied in practice, it was assumed that partial nitritation/Anammox can be operated even at sufficiently low sewage temperature (10–20°C) and dilute N sewage concentrations (<100 mg N/L) (Hendrickx et al., 2012).

Table 2.2 shows the removal efficiency with Anammox at 20°C (Hendrickx et al., 2012) and conversion values related to the partial nitritation/Anammox process.

Table 2.2: Efficiency and conversion values for partial nitritation/Anammox process

Process	Unit	Value used	Reference
Cold partial nitritation and Anammox			
• Overall N removal efficiency	% NH_4^+-N	90	Hendrickx et al. (2012)
• O_2 consumption	g O_2/g NH_4^+-$N_{removed}$	1.95[a]	–
• CO_2 need	g CO_2/g NH_4^+-$N_{removed}$	0.09[a]	–
• N_2 production	g N_2/g NH_4^+-$N_{removed}$	0.885[a]	–
• Nitrate production	g NO_3^-/g NH_4^+-$N_{removed}$	0.11[a]	–
• Biomass yield (N-removal)	g VSS/g NH_4^+-$N_{removed}$	0.05[a]	–
• COD in biomass	g COD/g VSS	1.42	Metcalf and Eddy (2004)
• N in biomass	g N/g VSS	0.09	Metcalf and Eddy (2004)
• P in biomass	g P/g VSS	0.02	Metcalf and Eddy (2004)
• COD removal efficiency (partial nitritation)	% of total COD	35[b]	–
• COD removal efficiency (Anammox)	% of total COD	5[b]	–
• Conversions for COD-removal, O_2 need, CO_2 production, and COD, N, P in biomass (see bioflocculation)			

[a] The following stoichiometric reactions are used for partial nitritation and Anammox (Cui, 2012):
Partial nitritation: $NH_4^+ + 0.75O_2 + HCO_3^- \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O$.
Anammox: $NH_4^+ + 1.32NO_2^- + 0.0664HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O$.
[b] Data from partial nitritation/Anammox N-removal from black water (de Graaff et al., 2011; de Graaff et al., 2010).

2.2.1.3 P recovery process

Conventional sewage treatment systems remove phosphorus either by chemical precipitation with iron or aluminum salts or by biological phosphorus removal via bacteria that take up phosphate and store it as poly-phosphate. In both cases the phosphorus ends up in the waste sludge and is no longer available for recovery. Phosphate recovery from wastewater is possible, for example by struvite precipitation or in a crystallactor (Piekema and Giesen, 2001) in which calcium phosphate granules are formed on sand particles. However, at low sewage temperatures

(10–20°C) and low phosphate concentrations (<10 mg PO_4^{3-}-P/L) these processes may not be economical and is the motivation for continued research efforts to develop novel cost-effective P-recovery technologies. Examples are electrochemical phosphate recovery (Kappel et al., 2013) and reversible adsorption of phosphate on iron oxides, e.g. Martin et al. (2009). Because it is expected that such technologies can achieve at least 90% phosphate removal efficiency, this efficiency was adopted for the present study (Table 2.3).

Table 2.3: Recovery efficiency for P recovery process

Process	Unit	Value used	Reference
P recovery			
• Overall P recovery (removal) efficiency	% PO_4^{3-}-P	90[a]	Design parameter

[a] Data from a review study done by de-Bashan and Bashan (2004).

2.2.1.4 Microalgae systems

Recovery of N and P using microalgae seems to be a suitable and efficient method for municipal wastewater (Boelee et al., 2012; Shi et al., 2007; Zamalloa et al., 2013). Microalgae are autotrophic organisms that use light as their source of energy for the production of microalgal biomass. Mixed microalgae and heterotrophic organisms for nutrients immobilization also allow COD to be removed. This is known as a combined treatment or symbiotic microalgae system (Boelee et al., 2012; Shi et al., 2007; Zamalloa et al., 2013). In this study, microalgae biofilms instead of a suspended algae pond were considered because of a lower mixing energy, harvesting cost, and surface area footprint. Although Boelee (2013) reported that the microalgal biofilms post-treatment of municipal wastewater effluent was not feasible for year-round application under Dutch climate conditions, still the concept of microalgae biofilms for COD and nutrients removal is interesting due to its feasibility to other regions, like Southeast Asian countries. Therefore, no final evaluation of this system will be presented in this case study with its focus on moderate climate conditions as found in the Netherlands. Under appropriate light and temperature conditions, the microalgae treatment/recovery provides lower aeration energy as compared to CAS systems because phototrophs can provide the heterotrophic bacteria with the oxygen to remove COD. Consequently, no extra aeration would be needed. Table 2.4 shows the removal and conversion efficiencies, and parameters that were used in the design of the microalgae systems.

Table 2.4: Efficiency, conversion and design parameter values for symbiotic microalgae process

Process	Unit	Value used	Reference
Symbiotic microalgae			
• N-target in effluent	mg NH_4^+-N/L	2.2	WFD, 2000/60/EC[a]
• CO_2 need	g CO_2/ g NH_4^+-$N_{removed}$	26.19[b]	–
• O_2 emission	g O_2/g NH_4^+-$N_{removed}$	22.67[b]	–
• Biomass yield	g VSS/g NH_4^+-$N_{removed}$	12.82[b]	–
• COD in microalgal biomass	g COD/g VSS	1.43	Collet et al. (2011)
• N in microalgal biomass	g N/g VSS	0.078[b]	–
• P in microalgal biomass	g P/g VSS	0.014[b]	–
• COD removal efficiency by heterotrophs	% CODbs	100	Design parameter
• Conversions for COD-removal, O_2 need, CO_2 production, and concentration of COD, N, P in biomass (see bioflocculation)			

[a] Requirements for discharges from the European water framework directive (WFD) 2000/60/EC.
[b] Assuming ammonium as N source, the following stoichiometric equation is used for microalgae (Boelee et al., 2012): $CO_2 + 0.7H_2O + 0.12NH_4^+ + 0.01H_2PO_4^- \rightarrow CH_{1.78}O_{0.36}N_{0.12}P_{0.01} + 1.19O_2 + 0.11H^+$.

2.2.1.5 Reference CAS system

In this study, a reference CAS system is defined for biological COD, N, and P removal. In addition, sludge is anaerobically digested to produce methane. Subsequently, CHP is used to convert methane into electricity and heat energy. The removal efficiency of organic matter during anaerobic digestion is assumed to be the same for both bioflocculation concentrate and CAS sludge waste; even though the bioflocculation concentrate sludge is estimated to give a higher yield in methane production than activated sludge. The removal and conversion efficiencies, and design specifications for the reference CAS system is shown in Table 2.5.

Table 2.5: Efficiency, conversion and design parameter values for the reference CAS system

Process	Unit	Value used	Reference
Conventional activated sludge			
• Total COD removal efficiency	%	85[c]	Design parameter
• Total N removal efficiency	% NH_4^+-N	90[c]	Design parameter
• Total P removal efficiency	% PO_4^{3-}-P	90[c]	Design parameter
• O_2 need (heterotrophs)	g O_2/g $CODb_{removed}$	0.51[a]	–
• O_2 need (nitrification)	g O_2/g NH_4^+-$N_{removed}$	4.32[b]	–
• O_2 need (biological P-removal)	g O_2/g $CODb_{removed}$	0.49[b]	–
• CO_2 need (nitrification)	g CO_2/g NH_4^+-$N_{removed}$	0.25[b]	–
• COD need (denitrification)	g COD/g NO_3^--N	3.92[b]	–
• COD need (biological P)	g COD/g PO_4^{3-}-$P_{removed}$	9.06[b]	–
• Biomass yield (COD-removal)	g VSS/g $CODb_{removed}$	0.40[a]	Metcalf and Eddy (2004)
• Biomass yield (nitrification)	g VSS/g NH_4^+-$N_{removed}$	0.16	Metcalf and Eddy (2004)
• Biomass yield (denitrification)	g VSS/g COD_{used}	0.30	Metcalf and Eddy (2004)
• Biomass yield (biological P)	g VSS/g COD_{used}	0.37[b]	–
• COD, N, P in biomass (see bioflocculation)			
• N_2 emission (denitrification)	g N_2/g NO_3^--N	0.92[b]	–
• CO_2 emission (heterotrophs)	g CO_2/g $CODb_{removed}$	0.70[a]	–
• CO_2 emission (biological P)	g CO_2/g $CODb_{used}$	0.70[b]	–
Anaerobic sludge digestion[d]			
CHP[d]			

[a] Assuming acetate as organic matter, the following stoichiometric equation is used for aerobic, heterotrophic oxidation of organic matter (Metcalf and Eddy, 2004):
$5CH_3COO^- + NH_4^+ + 5O_2 \rightarrow C_5H_7O_2N + 4H_2O + 5CO_2 + 4OH^-$.

[b] The following stoichiometric reactions are used for conventional nitrification/denitrification and biological P-removal in activated sludge systems, assuming acetate as COD (Metcalf and Eddy, 2004):
Nitrification: $NH_4^+ + 1.89O_2 + 0.08CO_2 \rightarrow 0.016C_5H_7O_2N + 0.95H_2O + 0.98NO_3^- + 1.98H^+$,
Denitrification: $12.5CH_3COO^- + 14.38NO_3^- + 14.38H^+ \rightarrow 1.22C_5H_7O_2N + 6.58N_2 + 12.5OH^- + 18.9CO_2 + 15.42H_2O$,
Biological P: $5CH_3COO^- + NH_4^+ + 0.1H_2PO_4^- + 4.875O_2 \rightarrow C_5H_7O_2NP_{0.1} + 5CO_2 + 4.05H_2O + 4.1OH^-$.

[c] With these removal efficiencies, a target effluent guideline of 125 mg COD/L, 10 mg N/L, and 1 mg P/L is possible.

[d] See Table 2.1.

2.2.2 Procedure for novel WWTP configurations

Figure 2.1 shows the five-step procedure to evaluate and select plant layouts for future municipal WWTPs. The first step is to identify the key performance indicators (KPIs) of future municipal WWTPs. New configurations should: 1) treat municipal wastewater such that the discharge guidelines are achieved; 2) be able to do so throughout the entire year; 3) maximize net energy yield and P recovery; and 4) minimize CO_2 emission. Only P recovery was considered in this study, as N recovery is less important than P recovery. At the low N concentrations used in this case study recovery would be too expensive and have too high an energy demand (Maurer et al., 2003).

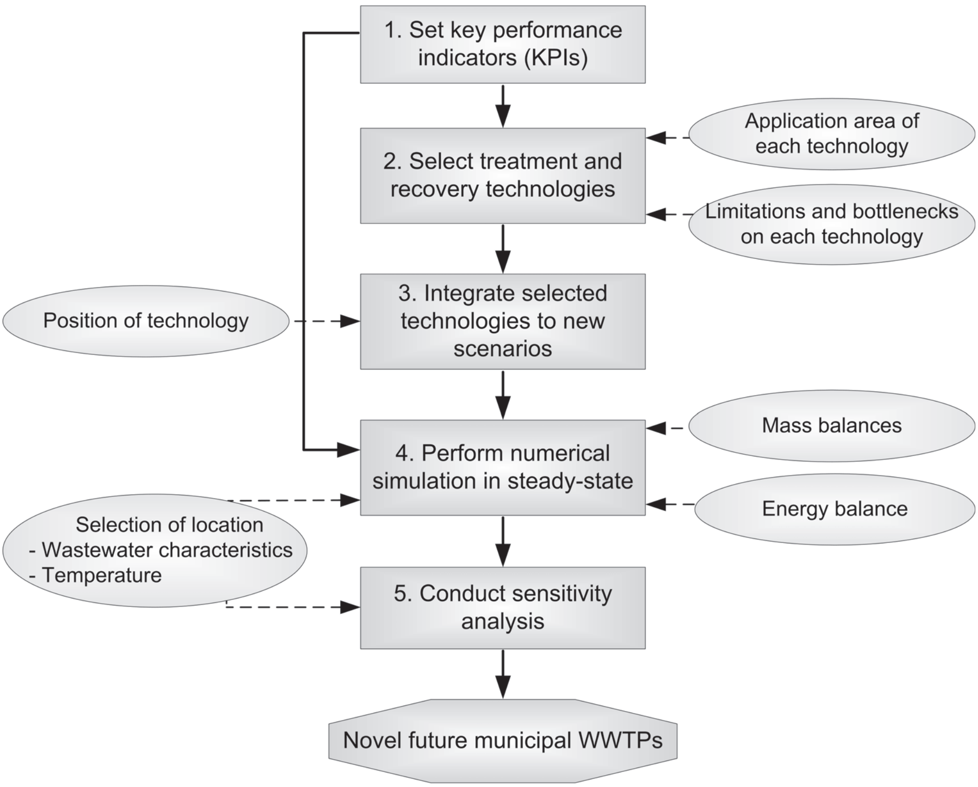

Figure 2.1: Procedure to investigate plant layouts of future municipal WWTPs

= process step, = input, = output

In the second step, wastewater treatment and recovery technologies were selected with respect to these KPIs. Four wastewater treatment and recovery processes, together with the reference aerobic COD, N, and P removal, are considered in this study, as mentioned above in Section 2.2.1.

In the third step, the four technologies were integrated into two new configurations, as shown in Figure 2.2. It is important to note that these two configurations were selected from 11 initial configurations (data not shown) with different positions of the process units and different recent technologies, for example microalgae as main treatment (Boelee et al., 2012), and low temperature upflow anaerobic sludge blanket and anaerobic digestion (Hendrickx et al., 2012). A preliminary selection from the 11 layouts showed that nutrient limitation and insufficient recovery efficiency were the main drawbacks of the 9 rejected configurations. Thus, only two configurations were further evaluated in this study. In Configuration 1 (Figure 2.2A), municipal wastewater, after pretreatment (screening and/or grit removal), is concentrated by bioflocculation. This pretreatment step removes heavy inert particles like sand and no significant changes in total COD, NH_4-N, and PO_4-P took place in this step. A large part of the particulate COD, is concentrated at a short hydraulic retention time (HRT) and SRT (Akanyeti et al., 2010), such that only a small part of biodegradable soluble COD (CODbs) is removed by aerobic mineralization. Likewise, a small fraction of available N and P will be incorporated in the heterotrophic biomass, and most of these nutrients will end up in the bioflocculation effluent. The next step consists of cold partial nitritation/Anammox to reduce N to levels that meet discharge guidelines; this is followed by phosphorus recovery. The bioflocculation concentrate is converted to methane in an anaerobic digester under mesophilic conditions (35°C). The methane production is converted to electricity and heat energy using a CHP unit. Even though the evaluation of the symbiotic microalgae system will not be presented in the case study, the scheme of this configuration could be found in Configuration 2 (Figure 2.2B). In Configuration 2, pretreatment, bioflocculation, anaerobic sludge digestion and CHP are similar to those in Configuration 1 except that a symbiotic microalgae system is used to assimilate N and P and includes a buffer tank to collect wastewater during the night when there is no microalgae activity (Richmond, 2004).

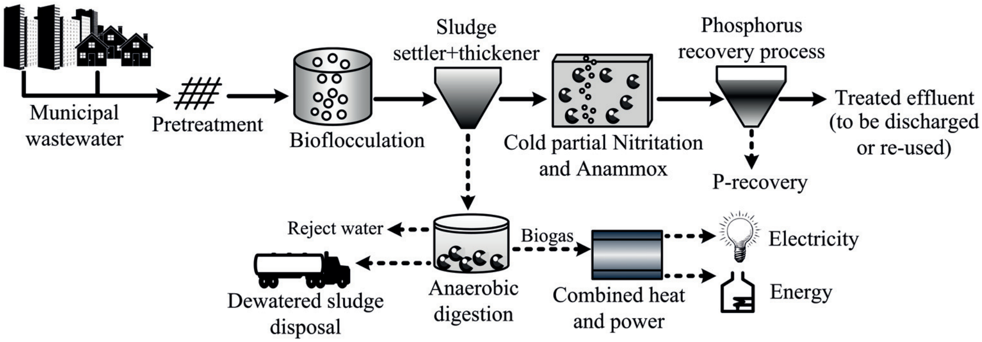

Figure 2.2A: Novel Configuration 1 with bioflocculation, partial nitritation and Anammox, P recovery process, anaerobic sludge digestion, and CHP

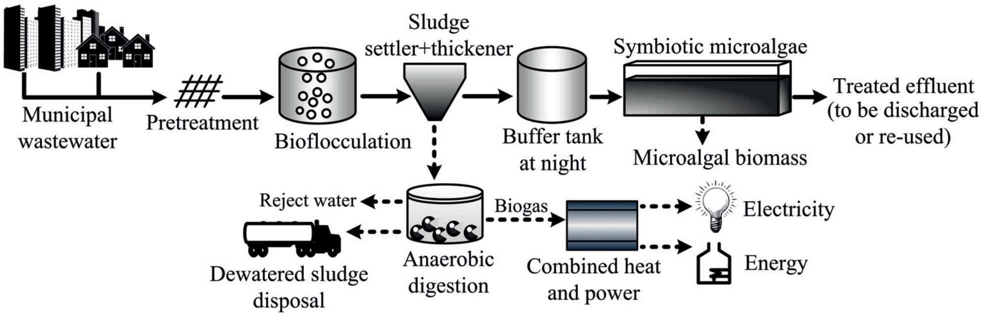

Figure 2.2B: Novel Configuration 2 with bioflocculation, symbiotic microalgae with heterotrophs, anaerobic sludge digestion, and CHP

In steps four and five of the procedure, the numerical calculations were performed (see Figure 2.1). Numerical simulation under steady-state conditions and quantification of the selected KPIs were performed based on the data shown in Tables 2.1–2.5. A sensitivity analysis was conducted in the last step. The consequences of changing a given input factor allow us to explore the feasibility of new configurations in other countries and regions. In this study, two input factors, i.e. temperature and wastewater compositions, were varied ±20% of the nominal values. As the ambient temperature would affect the required heating energy for anaerobic digestion, this becomes an interesting factor in our sensitivity analysis. Similarly, differences in wastewater composition affect both the recovery efficiencies as well as the total amount of resources that can be recovered.

2.2.3 Configuration assessment

Energy and mass balances, resource recovery, and effluent quality were calculated based on literature data and design specifications.

2.2.3.1 Mass balance

Stoichiometric equations were used to calculate the mass fluxes of COD, N and P in kg/day. Simple input–output models were built to relate the inflow and outflow through the use of mass balances for each selected process. The general form of the mass balance is given by:

$$\frac{dC_x V}{dt} = F_{x,in} C_{x,in} - F_{x,out} C_x + \sum_{k=1}^{q} P_{x,k} \qquad \textbf{(2.1)}$$

where VdC_X/dt is the accumulation of compound X (kg/day), F_x is the flow rate of compound X (m^3/day), C_x is the concentration of component X (kg/m^3). $\Sigma P_{x,k}$ is the consumption in k=1,…,q processes of component X (kg/m^3). In our case, component X refers to COD, N and P, respectively. In this study no accumulation of mass was assumed, consequently, the left hand side of Eq. 2.1 is set to zero, with $dC_X/dt = 0$ and $dV/dt = F_{in} - F_{out} = 0$, leading to $F = F_{in} = F_{out}$. All technology steps are assumed to scale linearly and no dynamics are included.

To calculate emissions, a global warming potential was based on both renewable CO_2, produced by biological processes, and non-renewable CO_2, produced by external electricity input with the assumption of 0.59 kg-CO_2/kWh (Frijns et al., 2008). No other significant greenhouse gas emissions, such as CH_4, CO, or N_2O that may be produced from the treatment processes, were considered for the environmental impact.

The energy balance, shown below, accounts for three terms: energy consumption, energy production, and net energy yield.

2.2.3.2 Energy consumption

To calculate energy consumption only aeration and heating were considered; pumping energy was not taken into account. Aeration energy for aerobic biological process and heating energy for anaerobic digester are the dominant energy needs to treat municipal wastewater (Pakenas, 1995). Energy required for aeration is calculated from the amount of oxygen consumed with an aeration efficiency rate of 1.5 kgO_2/kWh (Frijns et al., 2008; Metcalf and Eddy, 2004). Heating energy was calculated using the following equation:

$$\overline{H}_T = F * \rho * c_p * (T_{SETPOINT} - T_{in}) \qquad \textbf{(2.2)}$$

where $\overline{H}_T$ is the heating energy consumption (kWh/day), F is the volumetric influent flow rate (m^3/day), ρ is density of water (1 kg/L or 10^3 kg/m^3), c_p is a specific heat capacity of water (0.001167 kWh/kg/°C), $T_{SETPOINT}$ is the operational temperature of the anaerobic digester, which was set at 35°C, and T_{in} is wastewater temperature. In this study, the flow rate of thickener to anaerobic digestion for both Configuration 1 and the reference CAS is assumed to be the same. Thus, under this assumption heating energy consumption in anaerobic digestion requires the same amount for both configurations.

2.2.3.3 Energy production

The CHP unit efficiencies were assumed to be 38% for electricity production and 40% for heat recovery (Verstraete and Vlaeminck, 2011). The energy density of methane is 50–55.5 MJ/kg CH_4; therefore approximately 13.9 kWh/kg CH_4 was used (H2moves.eu, 2006).

2.2.3.4 Net energy yield

Net energy yield was calculated in kWh per m^3 of wastewater by subtracting the energy consumption from the total amount of heat (H_{AD}) and electricity (E_{AD}) production, and is given by the equation:

$$E_{net} = (H_{AD} + E_{AD}) - (H_T + H_{air}) \qquad \textbf{(2.3)}$$

where E_{net} is the net energy yield (kWh/m^3), H_{AD} is the amount heat production (kWh/m^3), E_{AD} is the amount of electricity production (kWh/m^3), H_T is the heating energy (kWh/m^3), and H_{air} is the aeration energy (kWh/m^3).

2.2.3.5 Sensitivity analysis

There are many different methods to conduct sensitivity analyses, such as differential sensitivity, subjective sensitivity, sensitivity index, and one-at-a-time sensitivity (Hamby, 1994; Saltelli et al., 2008). For a first indication of the sensitivities in this study, a one-at-a-time sensitivity analysis was conducted for Configuration 1 with respect to two factors: temperature and wastewater characteristics. Due to limited data of removal efficiencies at low temperatures (<20°C) for both bioflocculation and cold partial nitritation/Anammox, calculations with low temperatures may result in a relatively large uncertainty in simulation results. The energy consumption, energy production, and net energy yield were first calculated for the nominal values of the factors and then at values ±20% of nominal. The absolute value of the normalized sensitivity coefficient ($|S_{ij}|$) indicates the most and least sensitive factors and it provides a direction for future research. The normalized S_{ij} was calculated from:

$$S_{ij} = \frac{f_j(\bar{x}_i) - f_j(\underline{x}_i)}{\bar{x}_i - \underline{x}_i} * \frac{x_i}{f_j(x_i)} \tag{2.4}$$

where $f_j(\bar{x}_i)$ is the j th output value related to the maximum deviation point of the i th factor, $f_j(\underline{x}_i)$ is the j th output value related to the minimum deviation point of the i th factor, $f_j(x_i)$ is output value related to nominal value, $\bar{x}_i$ is maximum deviation point, $\underline{x}_i$ is minimum deviation point, and x_i is nominal value of the i th factor.

To further investigate the robustness of Configuration 1, a global sensitivity analysis (GSA), see for example Saltelli and Annoni (2010), was conducted with respect to temperature and wastewater characteristics. In this global sensitivity analysis, temperatures ranged from 15 to 25°C, total COD concentrations ranged from 289 to 647 mg/L, NH_4-N concentrations ranged from 19.1 to 54.6 mg/L, and PO_4-P concentrations ranged from 4.6 to 10.1 mg/L, where the intervals were obtained from Beheer Waterzuivering (2011). In the first step of the GSA, we standardized the four factors, such that each factor belongs to the interval [-1, +1]. In the second step, we sampled the resulting hyper box of step 1 for 1000 times, using a Latin hypercube sampling scheme, and conducted a simulation for each sampled combination of factors. In the last step, we carried out a second-order regression-based analysis, assuming for each output (heating energy, aeration energy, energy production, and net energy yield) the following relationship;

$$\bar{y} = y_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_{11} x_1^2 + \ldots + a_{44} x_4^2 + a_{12} x_1 x_2 + \ldots + a_{34} x_3 x_4 + e \quad \textbf{(2.5)}$$

with $\bar{y}$ is the simulated model output, y_0 is the reference output, $x_1,\ldots, x_4$ are the factors, e is the error term, and $a_1,\ldots,a_{34}$ are the regression parameters.

In compact matrix-vector form, suitable for further analysis, Eq. 2.5 can be written as;

$$\bar{y} = y_0 + \mathbf{a}^T\mathbf{x} + \mathbf{x}^T\mathbf{B}\mathbf{x} + e \quad \textbf{(2.6)}$$

with parameter vector $\mathbf{a}^T = [a_1, a_2, \ldots, a_4]$, vector of factors $\mathbf{x} = [x_1, x_2, \ldots, x_4]^T$, and symmetric matrix $\mathbf{B} = \begin{bmatrix} a_{11} & \frac{a_{12}}{2} & \frac{a_{13}}{2} & \frac{a_{14}}{2} \\ \frac{a_{12}}{2} & a_{22} & \frac{a_{23}}{2} & \frac{a_{24}}{2} \\ \frac{a_{13}}{2} & \frac{a_{23}}{2} & a_{33} & \frac{a_{34}}{2} \\ \frac{a_{14}}{2} & \frac{a_{24}}{2} & \frac{a_{34}}{2} & a_{44} \end{bmatrix}$, see Abusam et al. (2001).

For the estimation of $a_1,\ldots,a_{34}$, Eq. 2.5 can also be written as a linear regression model in matrix-vector form;

$$\mathbf{y} = \mathbf{\Phi}\boldsymbol{\theta} + \mathbf{e} \quad \textbf{(2.7)}$$

with $\mathbf{y} = [y_1, \ldots, y_{1000}]^T$, $\mathbf{\Phi}$ is the regression matrix, $\boldsymbol{\theta} = [y_0, a_1, \ldots, a_{34}]^T$, and $\mathbf{e} = [e_1, \ldots, e_{1000}]^T$.

It should be noted that each of the regression parameters is a sensitivity coefficient, which can be found from ordinary least-squares estimation, given the values of the sampled factors and corresponding simulated outputs, that is;

$$\hat{\theta} = \left(\Phi^T \Phi\right)^{-1} \Phi^T y \quad \textbf{(2.8)}$$

with $\hat{\theta}$ is a vector with 15 parameter estimates.

It should, however, be realized that sensitivities obtained from a global sensitivity analysis can be influenced by the parameter interval selected (Keesman, 1989; Shin et al., 2013).

2.2.4 Case study in the Netherlands

The novel configurations were simulated under Dutch conditions, and for 100,000 inhabitants treating 13,000 m^3 of wastewater per day. Average wastewater characteristics from 29 Dutch municipal WWTPs in 2010 were used (Beheer Waterzuivering, 2011). The concentrations of COD, N, and P are shown in Table 2.6. In the calculation of the heating energy, we assumed a wastewater temperature of 20°C.

Table 2.6: The average of 29 Dutch municipal wastewater in 2001–2010 and maximum potential energy

Constituent	Concentrations[a] (mg/L)	Maximum potential energy from organic oxidation[b] (kWh/m^3)
Organics (COD)		
Total (TCOD)	449.0	
biodegradable soluble (CODbs)[c]	78.6	0.30
biodegradable particulate (CODbp)[d]	260.0	1.00
non-biodegradable soluble (CODnbs)[e]	33.6	0.13
non-biodegradable particulate (CODnbp)[f]	76.8	0.30
ammonium (NH_4-N)	29.7	
phosphorus (PO_4-P)	6.7	
Total		1.73

[a] Based upon on determination of COD fractions of 17.5% for CODbs, 57.9% for CODpb, 17.1% for CODnbp, and 7.5% for CODnbs (Pasztor et al., 2009).
[b] Based upon a theoretical 3.86 kWh energy production/kg COD oxidized to CO_2 and H_2O (Owen, 1982).
[c] CODbs is soluble readily biodegradable organic material, which will be quickly assimilated into biomass and aerobic mineralized to CO_2.
[d] CODbp is slowly biodegradable organic material, it must first be dissolved by extracellular enzymes and therefore be assimilated and aerobic mineralized at slower rate compared to CODbs.
[e] CODnbs is non-biodegradable organic material, which will be found in the treated wastewater.
[f] CODnbp is non-biodegradable organic material, it will contribute to the total sludge production during wastewater has been treated (Metcalf and Eddy, 2004).

2.3 Results and Discussion

2.3.1 Novel configurations

Using the configuration assessment as introduced in Section 2.2.3, two novel configurations were developed to treat municipal wastewater with respect to energy, phosphorus recovery, and carbon footprint.

The calculations of Configuration 2 showed that in the summer months, with an average irradiance of 385 μmol photons/m^2/s over the day, with symbiotic microalgae treatment good N and P recoveries from sewage of 87% and 73%, respectively could be achieved. For COD and N also an effluent quality could be achieved that met their discharge guidelines. For P however, this was not possible because N became the limiting nutrient for microalgae growth. The N and P concentrations in the effluent in this study are in agreement with a study of Boelee et al. (2012), which also found N to be the limiting nutrient during symbiotic microalgae treatment. During the winter period microalgae treatment is not feasible for a temperate climate country like the Netherlands. The much lower temperature and an average irradiance in the winter period of 70 μmol photons/m^2/s (IET, 2014) prevent significant microalgae growth (Beardall and Raven, 2013; Boelee, 2013; Richmond, 2004). However, the positive results obtained during the summer months provide a strong indication that wastewater treatment systems based on symbiotic microalgae treatment may be feasible for tropical regions. However, this study was limited to Dutch conditions and therefore in the following this configuration will not be taken into consideration. The mass fluxes for COD, N, and P of Configuration 1 are shown in Figure 2.3.

The results from the primary treatment stream of Configuration 1 are comparable with the so-called Energy Factor configuration suggested by Stowa (2010); however, the side-stream processes differ. Still, further investigation of each process is required. For example, at present, a proven technology for optimal nitrite formation in partial nitritation at temperature below 20°C is not yet developed; therefore, remains a challenge. Recently, Hendrickx et al. (2012) suggested the use of limiting oxygen in the partial nitritation to keep it running at low temperatures. Further development of a P-recovery technology with minimal energy input and maximal recovery of high quality product is necessary.

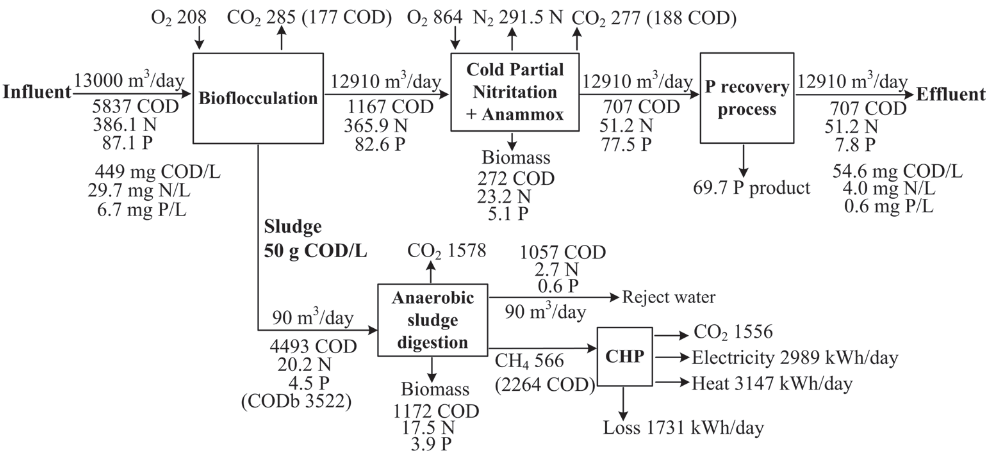

Figure 2.3: Mass balances (in kg/day) for nitrogen (N), phosphorus (P), and chemical oxygen demand (COD) in Configuration 1. COD in methane is 4 g CH_4-COD/g CH_4. The flows of biomass production in anaerobic digestion and cold partial nitritation/Anammox were not taken into account in the calculation. The corresponding calculation of mass fluxes of COD, N, and P can be found in Appendix A.

2.3.2 Numerical configuration assessment

The configuration assessment uses the KPIs as presented in Section 2.2.2.

2.3.2.1 Effluent quality

As demonstrated by the data in Table 2.7A, Configuration 1 can produce an effluent quality that meets the European urban wastewater treatment 91/271/EEC directive, i.e. maximum allowable concentrations for COD, N, and P of 125 mg-COD/L, 10 mg-N_{total}/L, and 1 mg-P_{total}/L, respectively (Council Directive, 1991). Ranges of effluent COD, the sum of nitrogen in ammonium and nitrate and phosphorus in phosphate concentrations from 29 Dutch municipal WWTPs in 2010 were reported with ranges of 29–72 mg COD/L, 2.2–9.2 mg NH_4-NO_3/L, and 0.3–3.0 mg PO_4-P/L (Beheer Waterzuivering, 2011). The effluent concentrations found in the reference CAS system and Configuration 1 are within these ranges. This indicates that the numerical model gives realistic results.

Table 2.7: Numerical results based on the selected key performance indicators (KPIs) for the novel configuration in comparison with the reference CAS system; (A) Effluent quality, operation applicable, and CO_2 emission, (B) Model performance on energy consumption, production and net energy yield

A

Configuration	Effluent quality (mg/L)			Whole year	CO_2 emission
	COD	N-(NH_4+NO_3)	PO_4-P	operation	(kg-CO_2/m^3)
Configuration 1	54.6	4.0	0.6	Yes	0.28
CAS	67.3	3.0	0.7	Yes	0.43

B

Configuration	Energy consumption/production/yield (kWh/m^3)				
	Energy consumption	Aeration	Heating	Energy production	Net energy yield
Configuration 1	0.23	0.11	0.12	0.47	0.24
CAS	0.37	0.25	0.12	0.29	-0.08[a]

[a] Negative value indicates that energy consumption is higher than energy production.

2.3.2.2 Whole year application

As with the CAS system, Configuration 1 is applicable the whole year through. Although the development of partial nitritation/Anammox at winter temperature (≤10°C) requires continued research effort, we believe a promising design for this treatment will be successfully achieved in the near future.

2.3.2.3 Maximization of net energy yield and P-recovery

Our implementation predicts an aeration energy consumption of 0.25 kWh per m^3 of wastewater for the reference CAS system (Table 2.7B), which is close to the value reported by McCarty et al. (2011) of 0.3 kWh per m^3. This again indicates the validity of our configuration assessment. Table 2.7B also shows that the total energy consumption of Configuration 1 was much lower than that of the CAS system, i.e. 0.23 and 0.37 kWh per m^3 of wastewater respectively. The volume of sludge fed to the digester was equal in both the CAS system and Configuration 1; therefore, the same amount of heating energy was needed to be able to operate anaerobic digester at 35°C. The lower energy consumption is attributable to the reduced aeration needs in Configuration 1 as most of the wastewater organic matter was diverted to the digester. This also explains why the energy production in Configuration 1 of 0.47 kWh per m^3 of wastewater is much higher than in the reference CAS system (0.29 kWh per m^3 of wastewater). The organic recovery (methane yield) increases from 24% in CAS system to 39% in Configuration 1 based on the total organic matter in the influent. Akanyeti et al. (2010) reported that at least 35% of the wastewater COD could be recovered as methane using the bioflocculation-digester concept the organic recovery difference between the studies can be explained by differences in the wastewater composition and operational parameters used. The net energy yield in Configuration 1 is 0.24 kWh per m^3 of wastewater, whereas in the CAS system no net energy is produced (net energy yield of -0.08 kWh per m^3 of wastewater).

In Configuration 1, 80% of the phosphorus in the influent is recovered, while in the CAS system all the phosphorus is wasted with the excess sludge. However, economically feasible P recovery from dilute wastewater streams still presents a technological challenge. Also, the quality of the P product remains an important issue as it may be polluted with heavy metals and organic micro-pollutants and may be of a lower quality compared to commercial products (Booker et al., 1999; de-Bashan and Bashan, 2004).

2.3.2.4 Minimization of CO_2 emission

As expected, the data assembled in Table 2.7A show that Configuration 1 will reduce CO_2 emission from 0.43 to 0.28 kg-CO_2 per m^3 of wastewater compared to the CAS system. This is because a larger fraction of COD is converted to methane rather than aerobically mineralized to CO_2.

2.3.3 Sensitivity analysis

Table 2.8 presents the values of the sensitivity coefficients of Configuration 1 in terms of energy. These coefficients were obtained after variations from the nominal value. Temperature and the wastewater composition were selected as input factors for this sensitivity study.

Table 2.8: Normalized sensitivity coefficient values of heating energy, aeration energy, energy production, and net energy yield calculated from ±20% variation in temperature, and fractions of wastewater composition. (Significant values are highlighted in bold.)

Absolute sensitivity coefficient	Heating energy	Aeration energy	Energy production	Net energy yield
Temperature	-0.5589	0.0000	0.0000	0.2798
Total COD in wastewater	**0.9999**	**0.3705**	**1.0001**	**1.2869**
NH_4-N in wastewater	0.0000	0.6295	0.0000	-0.2869
PO_4-P in wastewater	0.0000	0.0000	0.0000	0.0000
Fraction of CODbs in CODtotal	-0.0393	0.1598	-0.0237	-0.0995
Fraction of CODp in CODtotal	0.1179	-0.4794	0.0710	0.2984

As shown in Table 2.8, a ±20% variation in temperature, concentrations of NH_4-N and PO_4-P in wastewater, fraction biodegradable soluble COD in total COD (CODbs/COD ratio), and fraction particulate COD in total COD (CODp/COD ratio) did not give a significant difference for the energy terms. However, a 20% variation of total wastewater COD had a major impact on energy production and consumption.

For Configuration 1 this is further illustrated in Figure 2.4. The energy yield of Configuration 1 increased by 26% when the total COD increased by 20%–539 mg COD/L. This can be explained by higher methane production and lower amount of energy required for aeration and heating. For anaerobic digestion a constant settler capacity was assumed at 50 g-COD/L. Hence, the bioflocculated sludge is more concentrated and requires less heating input as the total volume is reduced. When total COD was increased by 20%, the methane production also increased by 20% while the heating energy decreased by 20%. In contrast, the aeration energy only decreased by 7% as a small amount of aeration is still required for the bioflocculation process.

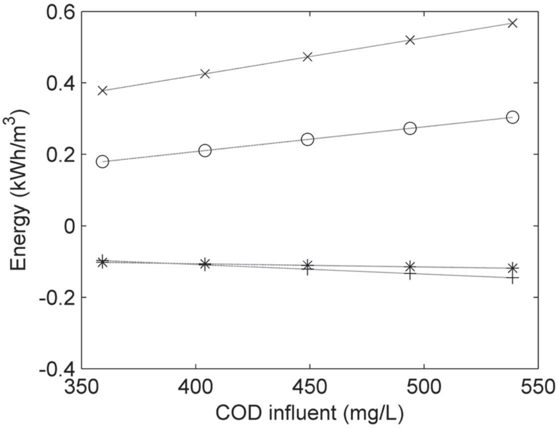

Figure 2.4: Normalized sensitivity coefficient values of heating energy (+), aeration energy (*), energy production (x), and net energy yield (o) calculated from ±20% and ±10% variation in total COD in influent (mg COD/L). The first, second, third, fourth and fifth points were calculated from -20%, -10%, nominal, +10%, and +20% variation, respectively. Negative values indicate that energy input is needed.

The sensitivities (estimates of a_1, a_2, ..., a_{34}) in Eq. 2.5 obtained from the global sensitivity analysis for Configuration 1 are presented in Table 2.9. The estimates in boldface clearly show that, under steady-state conditions, linear effects dominate; and that only the interaction between temperature and COD concentration effects heating and subsequently the net energy yield.

Given the estimates for each output (heating energy, aeration energy, energy production, and net energy yield) the second-order matrix **B** from Eq. 2.6 can be constructed. An eigenvalue decomposition of **B** may reveal ridges or valleys in the response surface and thus indicates which combination of parameters is sensitive. In our example, **B** contains many zeros and once again indicates that only the combination of temperature and COD concentration determines the heating energy and the net energy yield.

Table 2.9: Estimated values of heating energy, aeration energy, energy production, and net energy yield obtained from the global sensitivity analysis. The standard deviations are between brackets. (Significant values are highlighted in bold.)

Sensitivity coefficient	Heating energy	Aeration energy	Energy production	Net energy yield
Temperature	**4.07e-02 (1.56e-06)**	2.59e-06 (1.50e-06)	1.56e-06 (1.56e-06)	**4.07e-02 (1.54e-06)**
COD	**-5.23e-02 (1.56e-06)**	**-1.76e-02 (1.50e-06)**	**2.04e-01 (1.56e-06)**	**1.34e-01 (1.54e-06)**
NH_4-N	-2.16e-06 (1.62e-06)	**-4.14e-02 (1.56e-06)**	-4.59e-07 (1.62e-06)	**-4.14e-02 (1.59e-06)**
PO_4-P	-1.67e-07 (1.57e-06)	-1.41e-06 (1.51e-06)	3.03e-07 (1.57e-06)	8.44e-07 (1.55e-06)
T * COD	**1.74e-02 (2.70e-06)**	1.09e-06 (2.60e-06)	-1.87e-06 (2.70e-06)	**1.74e-02 (2.66e-06)**
T * NH_4-N	-2.31e-07 (2.84e-06)	-3.75e-06 (2.74e-06)	2.03e-07 (2.84e-06)	-1.73e-06 (2.80e-06)
T * PO_4-P	-2.90e-08 (2.64e-06)	-4.32e-06 (2.54e-06)	-3.88e-06 (2.64e-06)	1.06e-06 (2.60e-06)
COD * NH_4-N	4.66e-07 (2.75e-06)	4.09e-07 (2.65e-06)	-1.06e-06 (2.75e-06)	-4.72e-07 (2.71e-06)
COD * PO_4-P	4.49e-07 (2.62e-06)	4.24e-06 (2.52e-06)	-7.19e-07 (2.62e-06)	-6.45e-07 (2.58e-06)
NH_4-N * PO_4-P	2.54e-06 (2.79e-06)	-4.60e-07 (2.69e-06)	-1.83e-07 (2.79e-06)	-9.37e-08 (2.75e-06)
T^2	-1.09e-06 (3.11e-06)	-9.03e-06 (3.00e-06)	8.52e-07 (3.11e-06)	-3.15e-07 (3.07e-06)
COD^2	-7.23e-06 (3.10e-06)	-4.05e-07 (2.98e-06)	-1.64e-06 (3.10e-06)	-1.53e-07 (3.05e-06)
$(NH_4\text{-}N)^2$	4.32e-06 (3.13e-06)	-7.97e-06 (3.01e-06)	4.76e-07 (3.12e-06)	3.14e-06 (3.08e-06)
$(PO_4\text{-}P)^2$	4.06e-06 (3.05e-06)	3.59e-06 (2.94e-06)	-1.89e-06 (3.05e-06)	-1.04e-06 (3.00e-06)

2.4 Conclusions

This study has shown that it is possible to use a simple numerical simulation procedure to investigate future municipal WWTPs based on preconfigured key performance indicators for a selected country with specific wastewater characteristics and climate conditions. Using the Netherlands as an example for Western Europe and a moderate climate regime, it was found that:

- A promising configuration of future municipal WWTPs consists of (i) bioflocculation to concentrate organic matter, (ii) cold partial nitritation/Anammox to remove N, (iii) P recovery, and (iv) anaerobic digestion and CHP to produce methane and generate electricity and heat. However, the technologies of bioflocculation with anaerobic digestion, cold partial nitritation/Anammox, and P recovery should be further optimized and more fundamental knowledge about the integration of these process on municipal wastewater treatment is needed;

- The proposed configuration can produce effluent at a quality that meets the discharge guidelines and it is applicable to treat wastewater year-round;
- The net energy yield of the proposed configuration reached up to 0.24 kWh per m^3 of wastewater because both methane production increased and aeration energy decreased, whereas a net energy deficit was found in the reference CAS system;
- 80% of the phosphorus was expected to be recovered from the proposed configuration;
- CO_2 emission from the proposed configuration reduced by 35% as compared to the reference CAS system;
- A change in total COD concentration in the municipal wastewater resulted in a significant change in energy consumption and production; and
- With respect to second-order effects in a global sensitivity analysis, only the interaction between temperature and COD concentration determines the heating and thus also the net yield energy.

On the basis of the presented procedure, other feasible integrated configurations could be designed and analyzed to select the most promising configuration for specific wastewater characteristics and climate conditions. Subsequently, each process in such a promising configuration needs to be evaluated using dynamic modeling and to assess the system performance under time-varying conditions and to identify optimal operation conditions.

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Chapter 3

Glocal assessment of integrated resource recovery in municipal wastewater treatment

Abstract

This study aims at exploring the feasibility of two novel wastewater treatment configurations, including combined bioflocculation and anaerobic digestion but with different nutrient removal technologies, i.e. partial nitritation/Anammox or microalgae treatment. The feasibility of such configurations was investigated for 16 locations around the globe with respect to their net energy yield, nutrient recovery, CO_2 emission, and area requirements. The results quantitatively support the applicability of (cold) partial nitritation/Anammox in tropical regions and some locations in temperate regions. The configuration with microalgae treatment is only applicable the whole year round in tropical regions that are close to the equator line. Microalgae treatment has an advantage over the configuration with partial nitritation/Anammox with respect to consumption of aeration energy and recovery of nutrients, but not with respect to area requirements. The analysis showed that in Thailand, the net energy yield of both configurations is at least a factor 10 higher than conventional activated sludge systems, while CO_2 emission is at least 22% lower. A sensitivity analysis of the configuration employing microalgae treatment shows that microalgal biomass yield and nutrient concentrations in the sewage have a critical impact on the area requirement and effluent concentrations. This study quantitatively provides initial selection criteria for the feasibility of such configurations for different locations around the globe.

A modified version of this chapter is submitted for publication as:

Khiewwijit, R., Rijnaarts, H. , Temmink, H., Keesman, K. J., 2015. Glocal assessment of integrated resource recovery in municipal wastewater treatment.

3.1 Introduction

Sewage is commonly treated by conventional activated sludge (CAS) systems. However, these CAS systems cannot be considered sustainable because most of the organic matter is aerobically mineralized, the valuable nutrients nitrogen (N) and phosphorus (P) are not recovered and the treated water is not reused. Therefore, in recent years new municipal wastewater treatment plants (WWTPs) were proposed, which combine treatment with recovery of these resources (Khiewwijit et al., 2015b; Khiewwijit et al., 2015c; McCarty et al., 2011; Menger-Krug et al., 2012; Remy et al., 2014). Numerical simulation, based on literature information and experimental data, can be used to predict the feasibility of such novel treatment and recovery concepts. Khiewwijit et al. (2015c) used this approach to evaluate two novel WWTP configurations (Figure 3.1A) that have the potential to maximize energy recovery and recover phosphorus under Dutch conditions. They also compared these configurations to the CAS system (Figure 3.1B).

In Configuration 1, the diluted organic matter in municipal wastewater, after screening and grit removal, is concentrated by a bioflocculation process (Akanyeti et al., 2010; Faust et al., 2014). In experiments reported by Khiewwijit et al. (2015a), it was found that bioflocculation in a high-loaded membrane bioreactor (HL-MBR) could concentrate 75.5% of the sewage COD (chemical oxygen demand), whereas only 7.5% was mineralized into CO_2. They also found that only a small fraction of the sewage NH_4-N and PO_4-P ended up in the concentrate, and 90% of these compounds was conserved in the HL-MBR permeate. The bioflocculated sewage organic matter is subsequently converted to methane in a mesophilic anaerobic digester, followed by a combined heat and power (CHP) unit to convert the methane to electricity and heat. The effluent of the bioflocculation process is subsequently treated by (cold) partial nitritation/Anammox process for N removal. The P can be recovered, for example by struvite precipitation or by another low-cost technology (Cordell et al., 2011; Desmidt et al., 2015). In the study of Khiewwijit et al. (2015c) it was assumed that in the near future technologies which can recover P from diluted wastewater streams will become available. It was also assumed that such technologies can remove P down to levels that meet the discharge guidelines.

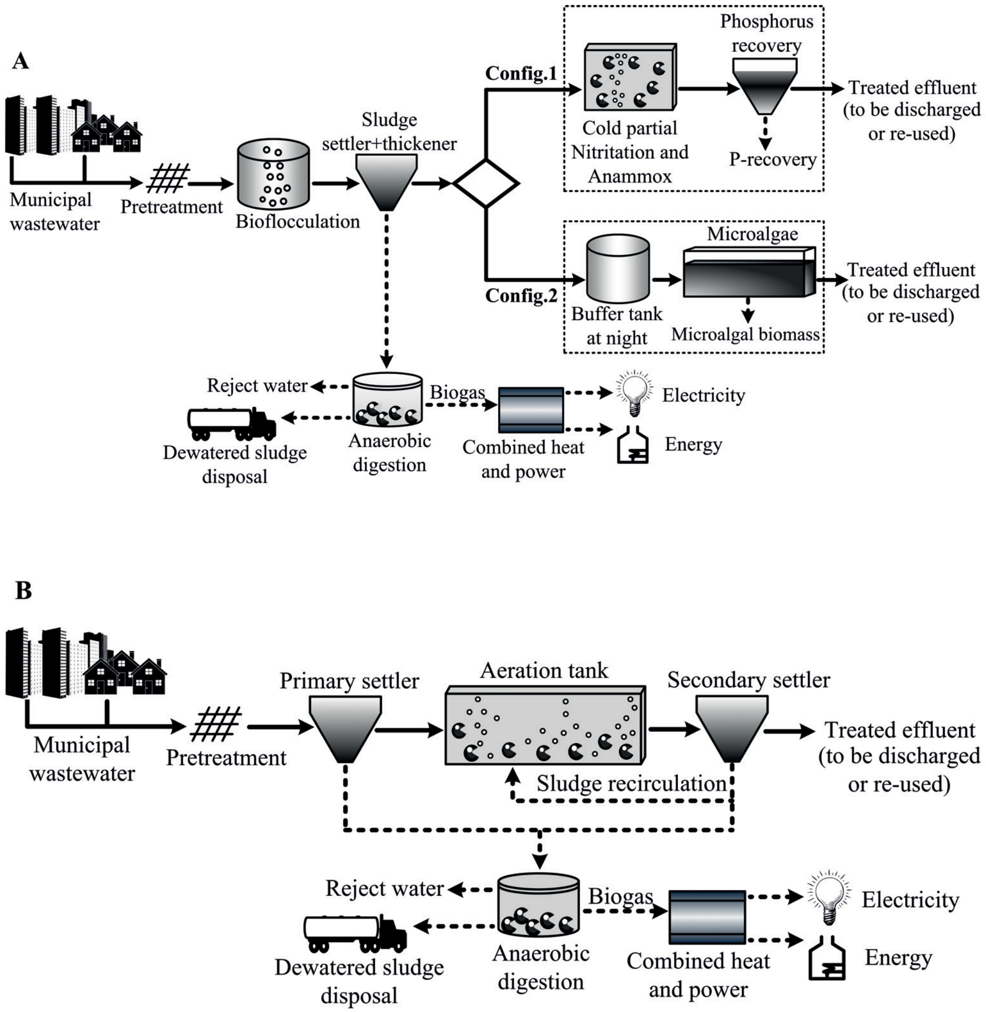

Figure 3.1: (A) Two novel configurations for municipal wastewater treatment, suggested by the study of Khiewwijit et al. (2015c), and (B) the CAS system. The solid lines indicate the processes of the mainstream treatment and dashed lines indicate processes of downstream solids treatment. is a decision block.

In Configuration 2, a similar approach with combined bioflocculation and anaerobic digestion of the bioflocculated organic matter is used. However, in this configuration the nutrients N and P in the effluent of the bioflocculation process are assimilated by microalgae. A buffer tank is required to store the bioflocculation effluent during the night when there is no microalgae activity. Microalgae treatment of municipal wastewater has been extensively studied because it reduces CO_2 emission and aeration energy otherwise needed for nitrification. The microalgal biomass can be used as a fertilizer (Uysal et al., 2015) or as a source for bioethanol, methane, biodiesel, and biohydrogen (Milledge and Heaven, 2014; Mu et al., 2014). Mahdy et al. (2015) showed the high potential of co-anaerobic digestion of sludge and microalgal biomass.

Khiewwijit et al. (2015c) evaluated the configurations of Figure 3.1A with respect to a number of key performance indicators (KPIs). It was found that Configuration 1 is the most promising configuration for the Netherlands, because it can:

1) treat wastewater year round;
2) produce an effluent at a quality that meets the discharge guidelines;
3) reduce CO_2 emission by 35% compared to the CAS system;
4) achieve a net energy yield up to 0.24 kWh per m^3 of wastewater, whereas the CAS system has a negative net energy yield of -0.08 kWh per m^3 of wastewater; and
5) recover 80% of the sewage P.

It was also demonstrated that Configuration 2 with microalgae treatment is not applicable in the Netherlands, because of a limited light availability, low temperature and low irradiance in the winter period. However, microalgae treatment still may be applicable in regions with a tropical climate (Olguín et al., 2003).

The objective of this study was to explore the feasibility of the above-mentioned municipal wastewater treatment configurations, including combined bioflocculation and anaerobic digestion with partial nitritation/Anammox or microalgae treatment for different locations around the globe, as we name here a glocal assessment analysis. Combined bioflocculation and anaerobic digestion were already analyzed in detail by Khiewwijit et al. (2015c) and therefore the present analysis mainly focused on the nitrogen removal technologies, i.e. (cold) partial nitritation/Anammox in Configuration 1 and microalgae treatment in Configuration 2.

3.2 Materials and Methods

3.2.1 Scenario-based analysis

The Excel-based model described by Khiewwijit et al. (2015c) with conversion efficiencies and design specifications for each of the processes in Configurations 1–2 and for the reference CAS system, was used for the calculations of the mass and energy balances under steady-state conditions.

Initially, under average annual temperature and light intensity conditions in Thailand the two configurations of Figure 3.1A were compared to the CAS system (Figure 3.1B) with respect to the KPIs. Thailand was selected as an example of a region with tropical climates, thus having a high potential for microalgae treatment. In Thailand winter and summer conditions with respect to temperature and light intensity are similar (Table 3.1). Therefore, to calculate the heating energy for anaerobic digestion at 35°C the average annual temperature was used. For calculation of the area requirement for microalgae treatment the average annual temperature and annual light intensity were used. The target N concentration in the effluent was 2.2 mg N_{total}/L, which obeys the maximum tolerable risk (MTR) guidelines used by the Dutch water boards. The P concentration in the effluent should always be below 1 mg P_{total}/L (Council Directive, 1991).

In a second step, for 16 selected locations worldwide the area requirements for a microalgae reactor were estimated in relation to seasonal changes of light intensity and temperature. The most promising wastewater treatment configurations for each of these locations were identified. Wastewater characteristics and required effluent quality were the same as used in the first step.

Finally, the effects of N and P sewage concentrations, microalgal biomass yield and biomass maintenance coefficient on the area requirement of a microalgae reactor and on effluent quality were examined in more detail for those locations where microalgae treatment could possibly be applied with respect to temperature, light availability and light intensity. A sensitivity analysis with respect to temperature and wastewater characteristics on cold partial nitritation/Anammox process was already conducted by Khiewwijit et al. (2015c) and thus it was excluded in this study. Minimum and maximum values for sewage NH_4-N of 20 and 35 mg N/L were used, respectively. For PO_4-P these values were 3 and 9 mg P/L, respectively (von Sperling, 2007).

3.2.2 Characteristics of municipal wastewater

The treatment configurations and the CAS system were evaluated for 100,000 inhabitants, treating a daily load of 13,000 m^3 of wastewater. Typical concentrations of organic matter, N and P in municipal wastewater were used: 600 mg COD/L, 25 mg NH_4-N/L and 5 mg PO_4-P/L (von Sperling, 2007).

3.2.3 Case study for different locations worldwide

Figure 3.2 shows 16 locations that were initially selected for the glocal assessment analysis.

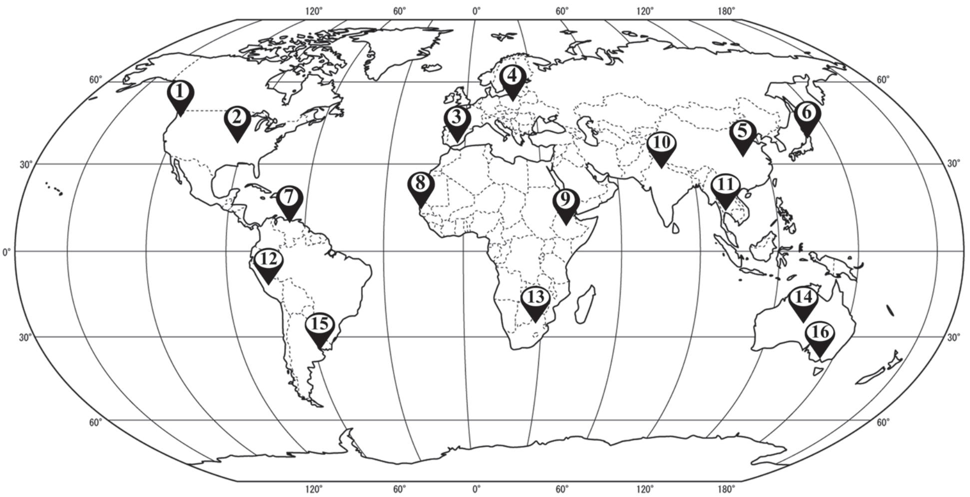

Figure 3.2: Map of the 16 selected locations used in this study; (1) USA, Washington, Seattle, (2) USA, Missouri, Kansas city, (3) Spain, Almeria, (4) Poland, Warsaw, (5) China, Xi'an, (6) Japan, Akita, (7) Venezuela, Caracas, (8) Senegal, Dakar, (9) Ethiopia, Addis Ababa, (10) India, New Delhi, (11) Thailand, Bangkok, (12) Peru, Huancayo, (13) South Africa, Pretoria, (14) Australia, Alice Springs, (15) Argentina, Buenos Aries, and (16) Australia, Melbourne

To select these locations, the globe was first divided into 36 regional groups with respect to degrees of longitude and latitude, where the globe was longitude-wise divided into 6 sub-regions of 60 degrees each, and latitude-wise divided into 6 sub-regions of 30 degrees each. The final 16 regional groups were obtained after subtraction of 12 regions (polar zones), located above 60 degrees latitude North and South with an average yearly temperature below 0°C, and 8 regions of which the surface is mainly covered by ocean from the 36 regions. A representative location, i.e. a well-known city in each of the 16 regions, was then selected based on available datasets given by PV Education (2015) and IET (2015).

Table 3.1: Average annual, summer and winter values of photon flux density (PFD) and temperature for the selected locations

Country/City	PFD[a,b], $mol/m^2/h$ ($\mu mol/m^2/s$)			Temperature[c], °C		
	Annual	Summer	Winter	Annual	Summer	Winter
Northern Hemisphere						
1. USA, Washington, Seattle	0.99 (275)	1.71 (475)	0.33 (91)	11.4	17.9	5.6
2. USA, Missouri, Kansas city	1.28 (354)	1.87 (520)	0.69 (192)	12.5	24.6	-0.4
3. Spain, Almeria	1.45 (402)	2.10 (583)	0.86 (240)	18.7	24.9	13.1
4. Poland, Warsaw	0.79 (220)	1.49 (414)	0.19 (52)	7.8	16.7	-0.7
5. China, Xi'an	1.15 (320)	1.50 (417)	0.80 (222)	13.4	25.7	1.0
6. Japan, Akita	0.95 (264)	1.29 (358)	0.43 (119)	11.1	22.3	0.7
Nearby Equator line						
7. Venezuela, Caracas	1.31 (363)	1.40 (389)	1.22 (339)	22.8	23.0	21.7
8. Senegal, Dakar	1.73 (481)	1.71 (476)	1.58 (438)	24.0	26.3	21.7
9. Ethiopia, Addis Ababa	1.56 (432)	1.68 (465)	1.23 (342)	16.3	17.3	15.7
10. India, New Delhi	1.32 (368)	1.59 (443)	0.98 (272)	25.0	32.6	15.2
11. Thailand Bangkok	1.56 (434)	1.78 (494)	1.77 (491)	28.2	29.0	26.3
12. Peru, Huancayo	2.04 (567)	2.22 (618)	1.93 (535)	10.1	10.9	8.9
Southern Hemisphere						
13. South Africa, Pretoria	1.62 (450)	1.93 (537)	1.30 (361)	18.6	22.7	13.0
14. Australia, Alice Springs	1.86 (518)	2.26 (628)	1.40 (388)	20.3	27.3	12.3
15. Argentina, Buenos Aries	1.37 (381)	2.00 (556)	0.74 (207)	17.7	24.0	11.6
16. Australia, Melbourne	1.18 (329)	1.87 (520)	0.57 (158)	14.3	19.3	9.3

[a] Solar radiation on the horizontal surface in $kWh/m^2/day$ taken from PV Education (2015), excluding China, Xi'an.

[b] China, Xi'an, solar irradiation on the horizontal surface in $Wh/m^2/day$ taken from IET (2015).

[c] Temperatures taken from Weatherbase (2015).

3.2.4 Photon flux density and temperature

Table 3.1 shows average annual, summer and winter values of photon flux density (PFD) and temperature for each selected location. All 16 locations were grouped into 3 different areas: (1) Northern hemisphere, i.e. locations above 30 degrees Northern latitude; (2) nearby the equator line; and (3) Southern hemisphere, which are locations close to and above 30 degrees Southern latitude. A regional dataset of surface solar radiation was taken from PV Education (2015) and IET (2015). The PFDs were then calculated following the steps in the study of Boelee et al. (2012), where it was assumed that 43% of the average photosynthetically active radiation (PAR), that is around 550 nm (400–700 nm), is utilized by microalgae. The temperatures were taken from Weatherbase (2015).

3.2.5 Area requirement for microalgae

The biomass productivity (P_{area} in g-dry weight/m^2/h) and area requirement (A in m^2/person) for a microalgae treatment reactor were calculated using the model and model parameters given in the studies of Tuantet (2015) and Zijffers et al. (2010), as shown in Eq. 3.1–Eq. 3.5:

$$C_{X,N} = \frac{N_{in} - N_{eff}}{F_N} \qquad \textbf{(3.1)}$$

$$r_{E,X} = \frac{PFD_{in}}{L * C_{X,N}} \qquad \textbf{(3.2)}$$

$$\mu_T = (r_{E,X} - m_{E,X}) * Y_{X,E} * f_T \qquad \textbf{(3.3)}$$

$$P_{area} = \mu_T * C_{X,N} * L \qquad \textbf{(3.4)}$$

$$A = \frac{F_W}{L * \mu_T} \qquad \textbf{(3.5)}$$

with $C_{X,N}$ the biomass density assuming that the amount of N rather than P determines the biomass production (g-dw/m^3), N_{in} and N_{eff} the concentrations of N in the influent and effluent, respectively (g N/m^3), F_N the fraction of N in microalgal biomass of 0.078 g-N/g microalgal biomass, $r_{E,X}$ the specific light intensity (mol photons/g-dw/h), PFD_{in} the supplied photon flux density (mol photons/m^2/h), L the light-path of photobioreactor (PBR) (m), μ_T the specific growth rate of microalgae (h^{-1}) with an effect of temperature expressed by a function of f_T, $m_{E,X}$ the biomass maintenance coefficient (mol photons/g-dw/h), $Y_{X,E}$ the biomass yield on light energy (g-dw/mol photons), P_{area} the biomass productivity (g-dw/m^2/h), A the area requirement (m^2/person), and F_W the flow rate (m^3/h/person).

Tuantet (2015) developed this model for (1) a high microalgal biomass concentration cultivated on human urine, (2) a short light path PBR to minimize the dark zone and (3) *Chlorella sorokiniana* as the main microalgae species. In the current study the same model was used because it is expected that similar microalgae species and reactor design can be used for municipal wastewater treatment. *Chlorella sorokiniana* is the most common microalgae species cultivated on municipal wastewater and has consistently high rates for nutrient removal and biomass productivity, as reviewed by Abinandan and Shanthakumar (2015) and Chen et al. (2011). Whereas Tuantet (2015) showed that P was the major factor limiting microalgae growth on human urine, in this study N is the limiting nutrient, as will be shown later.

Not only irradiance but also temperature affects microalgae growth (Eq. 3.3). Figure 3.3 shows the effect of temperature on growth rate of *Chlorella sorokiniana*. The effect of temperature on growth rate was calculated using the temperature function from the study of Slegers et al. (2013):

$$f_T = \left(\frac{T_{let} - T_w}{T_{let} - T_{opt}}\right)^{\beta} \exp\left(-\beta\left(\frac{T_{let} - T_w}{T_{let} - T_{opt}} - 1\right)\right) \qquad \textbf{(3.6)}$$

with f_T the effect of temperature on growth rate (dimensionless), T_{let} the lethal temperature of specific microalgae species use (°C), T_{opt} the optimal growth temperature of specific microalgae species (°C), and β the curve modulating constant related to temperature coefficient Q_{10}, which is the proportional change in growth rate with a 10°C rise in temperature (dimensionless).

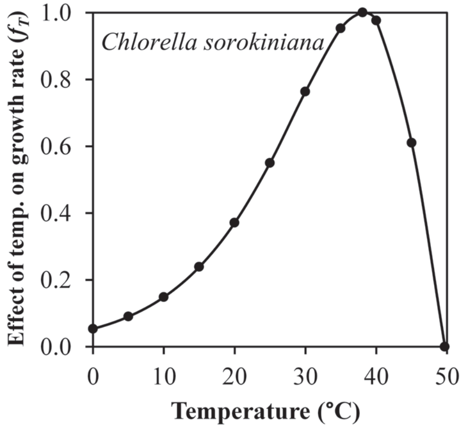

Figure 3.3: Effect of temperature on growth rate of *Chlorella sorokiniana*
If the temperature function $f_T = 0$, no growth is possible. If $f_T = 1$, growth is only influenced by sunlight intensity, independent of temperature.

3.2.6 Assumptions and parameter values

The following assumptions were made: (1) wastewater temperature is equal to the air temperature; (2) temperature does not affect the process of bioflocculation; (3) the anaerobic digester is controlled at a mesophilic temperature of 35°C; (4) photo-inhibition of the microalgae does not take place; and (5) cold partial nitritation/Anammox can be applied if the temperature is above 10°C. Lotti et al. (2014) showed that Anammox bacteria can be enriched at a temperature of 15°C. However, based on the work of Hendrickx et al. (2014), it is expected that in the near future it will be possible to apply partial nitritation/Anammox process at temperatures as low as 10°C. The system's and microalgae dependent parameters are given in Table 3.2.

Table 3.2: Parameters used in the calculations of area requirement for cultivation of microalgae

Parameter	Unit	Type of parameters		Reference
		System parameter	*Chlorella sorokiniana*	
N_{eff}	g N/m^3	2.2	–	Boelee et al. (2012)
$Y_{X,E}$	g-dw/mol photons	–	0.933	Tuantet (2015)
$m_{E,X}$	mol photons/g-dw/h	–	0.0068	Tuantet (2015) and Zijffers et al. (2010)
L	m	0.01	–	Tuantet (2015)
T_{opt}	°C	–	38.1	Morita et al. (2000)
T_{let}	°C	–	49.7	Morita et al. (2000)
β	(-)	–	1.6	Vona et al. (2004)

3.2.7 Sensitivity analysis

Differential sensitivity analysis was conducted for the area requirement of microalgae reactor in Configuration 2 with respect to two uncertain factors: the microalgal biomass yield on light energy ($Y_{X,E}$) and the microalgal biomass maintenance coefficient ($m_{E,X}$). The normalized sensitivity coefficients (dimensionless) indicate which of the two factors is most sensitive and provide directions for future research. The normalized sensitivity coefficient for a particular independent factor was obtained by taking the partial derivatives of the dependent variable with respect to the independent factor and scaled by the nominal values of the dependent variable and independent factor. Analytical expressions for the normalized sensitivity coefficients of area (A) with respect to $Y_{X,E}$ and $m_{E,X}$ are given by (see Appendix B for details):

$$S_{A,Y_{X,E}} = \frac{-F_W * \bar{Y}_{X,E}}{L*\left(\frac{PFD_{in} * F_N}{L*\left(N_{in} - N_{eff}\right)} - m_{E,X}\right) * f_T * \left(Y_{X,E}\right)^2 * \bar{A}} \qquad \textbf{(3.7)}$$

$$S_{A,m_{E,X}} = \frac{F_W * \bar{m}_{E,X}}{L * \left(\frac{PFD_{in} * F_N}{L * \left(N_{in} - N_{eff} \right)} - m_{E,X} \right)^2 * f_T * Y_{X,E} * \bar{A}} \quad \textbf{(3.8)}$$

with $S_{A,Y_{X,E}}$ the nominalized sensitivity coefficient of area requirement on $Y_{X,E}$, $S_{A,m_{E,X}}$ the nominalized sensitivity coefficient of area requirement on $m_{E,X}$, $\bar{Y}_{X,E}$ the nominal value of $Y_{X,E}$, $\bar{m}_{E,X}$ the nominal value of $m_{E,X}$, and $\bar{A}$ the area requirement related to the nominal values of each factor.

A one-at-a-time sensitivity analysis was used to quantify the changes in effluent quality and area requirement by varying sewage N and P concentrations. As mentioned before, NH_4-N concentrations varied from 20 mg N/L (N_{min}), 25 mg N/L ($N_{typical}$) to 35 mg N/L (N_{max}). PO_4-P concentrations varied from 3 mg P/L (P_{min}), 5 mg P/L ($P_{typical}$) to 9 mg P/L (P_{max}). Calculations of area requirement were performed based on average annual light intensity and temperature conditions.

3.3 Results and Discussion

3.3.1 Scenario-based analysis

The study of Khiewwijit et al. (2015c) showed that year round wastewater treatment with microalgae is not feasible in the Netherlands. Therefore, an initial quantitative scenario-based analysis of the two new WWTP configurations and the CAS system was conducted for Thailand, because it is expected that in Thailand both partial nitritation/Anammox and microalgae treatment can be applied throughout the entire year. Table 3.3 shows the KPIs for the three WWTP systems when operated in Thailand.

Table 3.3: Numerical results based on the key performance indicators (KPIs) for Configurations 1 and 2 in comparison to the CAS system, using Thailand as a case study; (A) Energy consumption, energy production and net energy yield, (B) Nutrient recovery and CO_2 emission

A

Configuration	Energy consumption/production/yield (kWh/m^3 of wastewater)				
	Energy consumption	Aeration	Heating	Energy production[a]	Net energy yield[b]
Configuration 1	0.18	0.11	0.07	0.63	0.45
Configuration 2	0.10	0.03	0.07	0.63	0.53
CAS	0.36	0.29	0.07	0.40	0.04

[a] This energy production includes both electricity and heat energy.
[b] This net energy yield is calculated based on energy consumption only aeration and heating, other energy needs of such as pumping, lighting and dewatering are not taken into account.

B

Configuration	Nutrient recovery (as 100% of initial amount)		CO_2 emission/consumption (kg-CO_2/m^3 of wastewater)	
	N	P	CO_2 emission	CO_2 consumption
Configuration 1	0	72	0.38	0
Configuration 2	70	65	0.35	-0.63[c]
CAS	0	0	0.49	0

[c] Negative values indicates that CO_2 consumption is mainly for a microalgae reactor.

3.3.1.1 Energy and nutrient recovery

While in the CAS system the major fraction of sewage organic matter is aerobically mineralized, in Configurations 1 and 2 most of this organic matter is distributed to the anaerobic digester. This explains why in Configurations 1 and 2 significantly more methane is produced, and thus more electricity and heat energy are generated than in the CAS: 0.63 kWh per m^3 of wastewater compared to 0.40 kWh per m^3 for the CAS system (Table 3.3A). Table 3.3A also shows that for all configurations the same amount of energy was needed to heat up the anaerobic digester, because the amount of water going to the anaerobic digester was assumed to be the same for all configurations. Because during bioflocculation oxidation of organic matter is minimized, the total aeration energy of Configuration 1 (0.11 kWh/m^3 of wastewater) and of Configuration 2 (0.03 kWh/m^3 of wastewater) was much lower than the aeration energy needed for the CAS system (0.29 kWh/m^3 of wastewater). Remark that in theory, the oxygen that is produced by the microalgae in Configuration 2 could be used in the bioflocculation unit, further reducing the aeration energy that is needed in this configuration. However, this is not currently technologically feasible. The higher aeration energy in Configuration 1 compared to Configuration 2 can be explained by the oxygen that is needed for partial nitritation (Fux and Siegrist, 2004).

When applied under Thai conditions, the net energy yield of Configuration 2 (0.53 kWh/m^3 of wastewater) is slightly higher than for Configuration 1 (0.45 kWh/m^3 of wastewater) and at least a factor 10 higher than for the CAS system. It should be noted that in these results energy consumption for pumping, thickening and dewatering was not taken into account and that to harvest microalgal biomass also a considerable amount of energy is required (Chen et al., 2011; Collet et al., 2011).

Table 3.3B shows that with Configuration 1 72% of the sewage P was recovered, while in the CAS system all the P and N were wasted with the excess sludge or by N_2 emission, respectively. In Configuration 2, 70% of the sewage N and 65% of the sewage P was assimilated by microalgae. This implies that Configuration 2 employing a microalgae reactor presents as a promising option for municipal wastewater treatment with respect to amounts of nutrient recovery.

3.3.1.2 CO_2 emission

Table 3.3B shows that in Thailand CO_2 emission for the CAS system was 0.49 kg CO_2/m^3 of wastewater. In Configuration 1, CO_2 emission was 22% lower (0.38 kg CO_2/m^3). In Configuration 2, the CO_2 emission was 0.35 kg CO_2/m^3 of wastewater. Also, in this configuration the microalgae need 0.63 kg CO_2/m^3 to be able to grow. Theoretically, this CO_2 consumption could be supplied by the bioflocculation and anaerobic digester. However, similar to the oxygen transfer from microalgae reactor to the bioflocculation unit this currently is technologically not feasible.

3.3.1.3 Area requirement

Based on the results presented in Table 3.3, Configuration 2 with microalgae treatment seems to be the most promising design for future municipal WWTPs in Thailand and in other tropical regions. However, the model calculations show that a microalgae reactor requires an area of 2.2 m^2/person. This is similar to the 2.1 m^2/person found by Boelee et al. (2012) for a microalgae biofilms reactor that was applied for nutrient removal after a high-rate activated sludge process to remove organic pollutants. A typical CAS system only requires 0.2–0.4 m^2/person (Boelee et al., 2012). Thus, microalgae treatment may only be a viable option in rural areas. On larger scales, i.e. located in or nearby cities, land availability and costs are limiting factors. This implies that microalgae treatment only would be attractive if high value products, such as carotenoids, aquaculture feed and dietary supplement can be produced by the microalgae (Enzing et al., 2014). It is recognized however that in this case contamination of the microalgal biomass with wastewater pollutants, for example pathogens, heavy metals and organic micropollutants could present a serious problem.

3.3.2 Area requirement for different locations worldwide

The productivity of microalgae is location specific, because it is largely determined by light intensity and availability and by temperature (Slegers et al., 2013). To investigate this in more detail, microalgal biomass productivity and area requirement were calculated for 16 locations around the globe, with their different seasonal conditions (Table 3.1). Figure 3.4 shows biomass productivity and area requirement for each of these locations as a function of average annual, summer and winter temperature and light intensity.

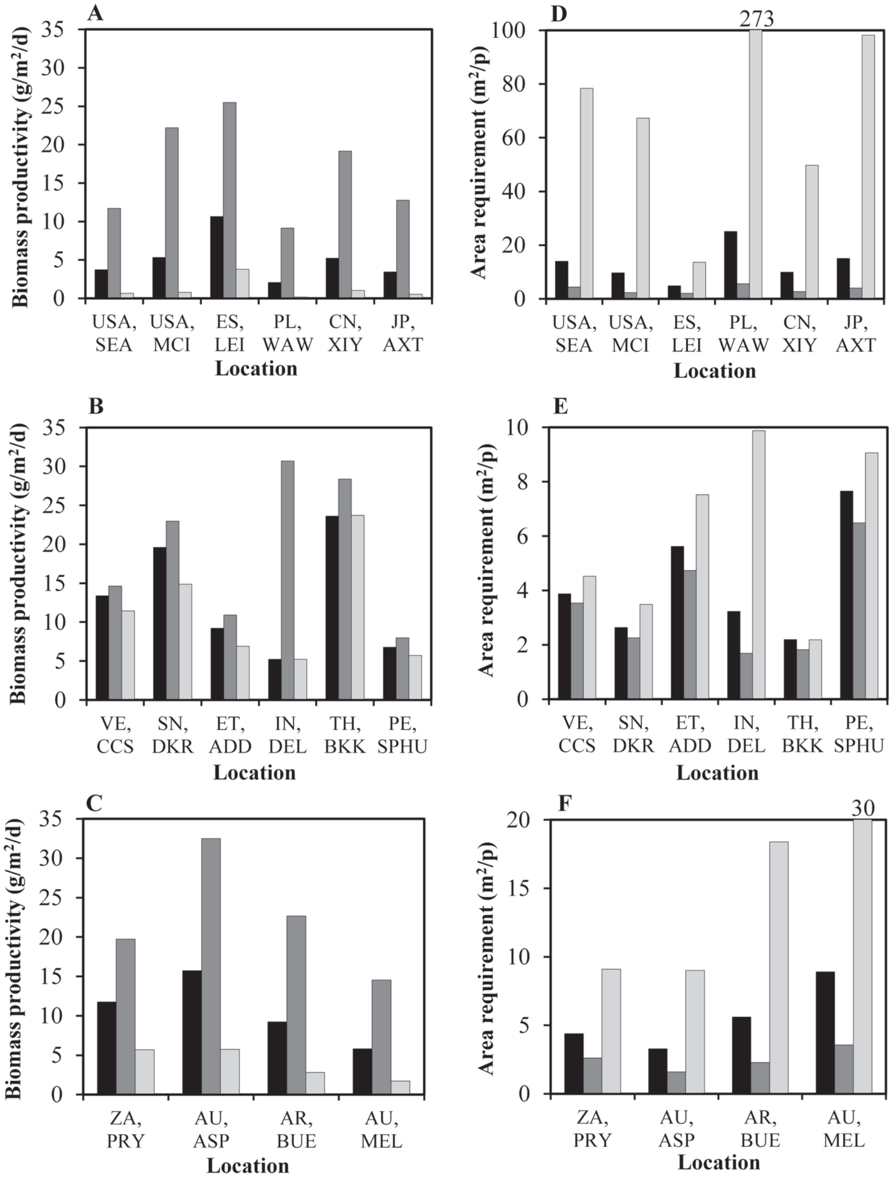

Figure 3.4: Comparison of calculated (A, B, C) biomass productivity and (D, E, F) area requirements for all 16 locations under different seasonal conditions; (black) annual, (grey) summer, (light grey) winter. Locations are grouped into; (A, D) Northern hemisphere, (B, E) nearby the equator line and (C, F) Southern hemisphere. (Numbers represent area requirements for values higher than presented in Y-axis.)

In the Northern hemisphere (Figure 3.4A) biomass productivities were very different (0.2–25.5 g-dw/m^2/d) between summer and winter. The area requirement ranged between 2 and 6 m^2/person for the summer period and between 14 and 273 m^2/person for the winter period (Figure 3.4D). The model in this study allowed microalgae growth at temperatures below 5°C, but it is very unlikely that microalgae can really grow at such temperatures. Therefore, area calculations at very low temperatures may result in a relatively large uncertainty in the simulation results. Nevertheless, because of the large area requirements in the winter periods it can be concluded that Configuration 2 employing a microalgae reactor is not feasible for locations in the Northern hemisphere.

In contrast, microalgae treatment seems to be applicable for locations nearby the equator line. For the winter period, the lowest area requirement was found for Thailand - Bangkok with 2.2 m^2/person, followed by Senegal - Dakar (3.5 m^2/person), Venezuela - Caracas (4.5 m^2/person), Ethiopia - Addis Ababa (7.5 m^2/person), Peru - Huancayo (9.1 m^2/person), and India - New Delhi (9.9 m^2/person). Thus, the area requirements for configuration based on microalgae treatment always are much higher than for CAS systems (0.2–0.4 m^2/person), but are comparable to the area for other low-cost wastewater treatment systems such as constructed wetlands of 3.5–7 m^2/person (Rousseau et al., 2004). Interestingly, Figure 3.4E shows that in India the area requirement in the winter period was almost 5 times higher than in the summer period (1.7 m^2/person). Thus, when winter conditions are very different from summer conditions, for instance more than a 10°C difference in temperature, microalgae treatment could be a promising option for municipal wastewater only for the summer period, while the CAS system or Configuration 1 is still needed for the winter period. However, this may not be economically feasible and thus Configuration 1 with (cold) partial nitritation/Anammox would be an attractive option to treat wastewater throughout the entire year.

With respect to the Southern hemisphere, a microalgae treatment is only applicable for tropical regions. The area requirements for the winter period for South Africa - Pretoria and Australia - Alice Springs were 9.1 and 9.0 m^2/person, respectively. Similar to India, on these locations microalgae treatment only seems to be possible in the summer period. In Argentina - Buenos Aries and Australia - Melbourne a microalgae treatment is not realistic, because the high area requirements are as high as 18 and 30 m^2/person in the winter, respectively (Figure 3.4F).

Based on the results above, it was concluded that Configuration 2 with microalgae treatment is only feasible for tropical locations, for example Venezuela - Caracas, Senegal - Dakar, Ethiopia - Addis Ababa, Thailand - Bangkok and Peru - Huancayo, where light intensity at the winter period is above 340 μmol photons/m^2/s and differences in water temperature between summer and winter are less than 5°C. Configuration 1 with (cold) partial nitritation/Anammox for N removal is only feasible at locations where the winter water temperature is above 10°C (Hendrickx et al., 2014). This concerns tropical regions and some locations in temperate regions, such as Spain - Almeria, India - New Delhi, South Africa - Pretoria, Australia - Alice Springs, and Argentina - Buenos Aries. However, a technological bottleneck may be partial nitritation at low temperatures (Hao et al., 2002).

Figure 3.5 summarizes the feasibility of applying Configuration 1 or 2 for different locations. In case Configurations 1 and 2 are not feasible, for example for Washington - Seattle, Missouri - Kansas city, Poland - Warsaw, China - Xi'an, Japan - Akita, and Australia - Melbourne, CAS systems should be applied because they works throughout the entire year. It should, however, be realized that at very low water temperatures also CAS systems may not work during the winter period because of a reduced nitrification efficiency (Kim et al., 2008).

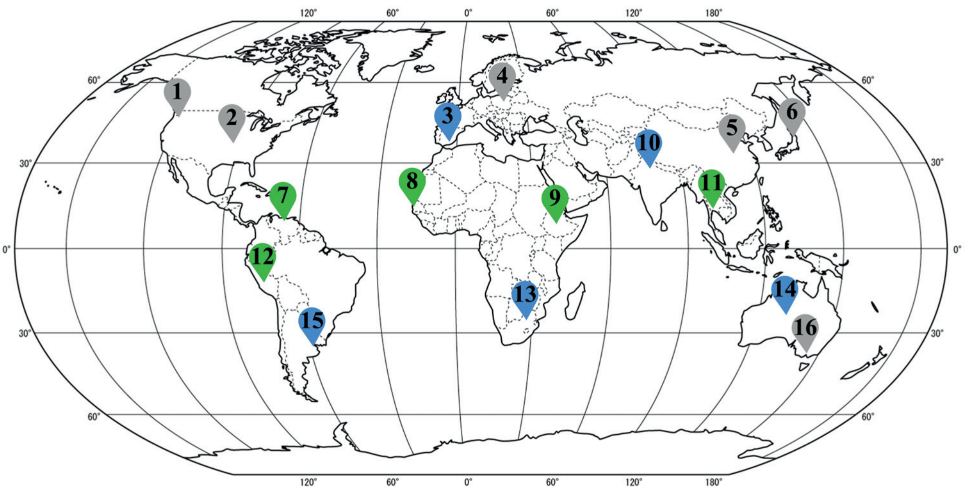

Figure 3.5: Map of the 16 selected locations used in this study with the most promising candidate for municipal wastewater treatment; (blue) Configuration 1 with (cold) partial nitritation/Anammox, (green) Configuration 2 with microalgae, and (grey) the CAS system

3.3.3 Sensitivity analysis

A sensitivity analysis was performed for Configuration 2 with respect to wastewater composition, microalgal biomass yield and microalgal biomass maintenance. This sensitivity analysis was conducted only for Venezuela - Caracas, Senegal - Dakar, Ethiopia - Addis Ababa, Thailand - Bangkok, and Peru - Huancayo, where microalgae treatment is a promising concept.

3.3.3.1 Microalgal biomass yield and maintenance coefficient

The microalgal biomass yield has a major impact, while microalgal biomass maintenance only had a minor effect on the area requirements (Figures B.1–B.2 of the Appendix B). Figure 3.6 shows the effect of microalgal biomass yield on the area requirements for different (average) annual temperatures and light intensities.

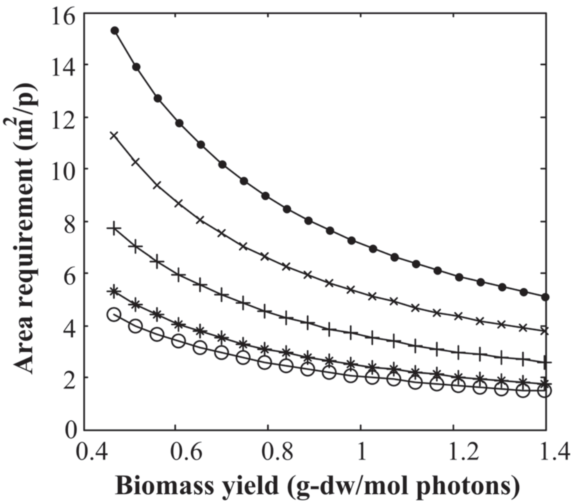

Figure 3.6: Area requirements in relation to different microalgal biomass yield values for the five potential locations, that are applicable for Configuration 2 with microalgae treatment; (+) Venezuela - Caracas, (*) Senegal - Dakar, (x) Ethiopia - Addis Ababa, (○) Thailand - Bangkok, and (●) Peru - Huancayo. (Results represent the area requirement with respect to annual temperature, annual light intensity, and typical wastewater composition: 600 mg COD/L, 25 mg NH_4-N/L and 5 mg PO_4-P/L.)

Clearly, when more biomass can be grown per mole of photons, less area is needed. Kliphuis et al. (2010) reported a theoretical maximum biomass yield on nitrate of 1.57 g-dw/mol photons. A similar value can be anticipated on ammonium as nitrogen source. In this study, a typical biomass yield of 0.933 g-dw/mol photons was used. However, this yield depends on the microalgae species and/or reactor type (Boelee et al., 2014) and can cause huge differences in area requirements. For example, in Peru the area requirement would increase from 7.7 m^2/person at a biomass yield of 0.933 g-dw/mol photons to almost 16 m^2/person at 0.450 g-dw/mol photons. This demonstrates that interpretation of the model results should be done with great care, and more experimental data about the biomass yield is required before conclusions can be drawn about the applicability of microalgae treatment.

Unlike the effect of biomass yield, the microalgal maintenance coefficient did not give significant difference in the area requirement (Figure B.2). This can be explained by the low N concentrations in municipal wastewater compared to other wastewater sources. This results in a low biomass concentrations (Eq. 3.1) with a high specific light intensities, i.e. a large fraction of the light is available for the microalgae (Eq. 3.2) and therefore a maintenance requirement, which is insignificant compared to the growth rate of the microalgae (Eq. 3.3). For example, after bioflocculation process a concentration of 21 mg N/L would be assimilated by microalgal biomass and this would lead to a low biomass density of approximately 0.3 g-dw/L. Other N sources such as urine have much higher N concentrations and the biomass density could be as high as 14.2 g-dw/L (Tuantet, 2015).

3.3.3.2 NH_4-N and PO_4-P concentrations

Table 3.4 gives effluent quality and area requirements for a range of different concentrations of N and P (von Sperling, 2007). The numbers in boldface clearly show that N and P concentrations have a major impact on the effluent quality. If the concentration of PO_4-P in wastewater would increase from 5 to 9 mg P/L, N rather than P would become the limiting nutrient for microalgae growth. This implies that P in the effluent can no longer meet the effluent guideline of 1 mg P_{total}/L and additional post-treatment would be needed. In contrast, if the concentration of NH_4-N in wastewater would increase from 25 to 35 mg N/L, while the concentration of PO_4-P would decrease from 5 to 3 mg P/L, P rather than N becomes the limiting nutrient. In this case additional N removal is required (van der Steen et al., 2015).

Table 3.4: Comparison of numerical results based on effluent quality (mg/L) and area requirement (m^2/person) for microalgae cultivation with given annual PFD and annual temperature, as mentioned in Table 3.1, and based on a range of sewage concentrations of NH_4-N and PO_4-P. NH_4-N concentrations varied from 20 mg N/L (N_{min}), 25 mg N/L ($N_{typical}$) and 35 mg N/L (N_{max}). PO_4-P concentrations varied from 3 mg P/L (P_{min}), 5 mg P/L ($P_{typical}$) and 9 mg P/L (P_{max}). Significant values are highlighted in bold.

Wastewater characteristic	N_{min}, P_{min}	N_{max}, P_{min}	N_{min}, P_{max}	N_{max}, P_{max}	$N_{typical}$, $P_{typical}$
Effluent quality					
NH_4-N (mg N/L)	5.64	**20.78**	2.20	2.20	2.20
PO_4-P (mg P/L)	0.15[a]	0.15[a]	**5.57**	**2.78**	0.60
Area requirement (m^2/person)					
1. Venezuela, Caracas	2.3	2.3	2.9	5.8	3.9
2. Senegal, Dakar	1.6	1.6	2.0	3.9	2.6
3. Ethiopia, Addis Ababa	3.3	3.3	4.3	8.4	5.6
4. Thailand, Bangkok	1.3	1.3	1.7	3.3	2.2
5. Peru, Huancayo	4.5	4.5	5.8	11.4	7.7

[a] P becomes the limiting nutrient; therefore, the biomass density was calculated based on a fraction of P in microalgal biomass of 0.0145 g-P/g algal biomass (Tuantet, 2015) and P-target in effluent was 0.15 mg P/L (Boelee et al., 2012).

Table 3.4 also shows that the composition of NH_4-N and PO_4-P in the sewage has a strong impact on the area requirement. The area requirement becomes about 40% lower when the concentrations of both NH_4-N and PO_4-P changed from typical to minimum values and approximately 50% higher when concentrations change from typical values to maximum values. At a minimum PO_4-P concentration of 3 mg P/L, a higher NH_4-N does not necessarily result in a higher area requirement, because P becomes the limiting nutrient. Nevertheless, at a maximum PO_4-P concentration of 9 mg P/L and a maximum NH_4-N of 35 mg N/L, the cultivation area was about 2 times the area needed at a maximum PO_4-P concentration and a minimum NH_4-N concentration of 20 mg N/L. These results indicate that, in addition to light intensity and temperature conditions, the potential of microalgae treatment is strongly determined by the concentrations of NH_4-N and PO_4-P in the sewage.

3.4 Conclusions

The feasibility of two novel municipal wastewater treatment configurations was investigated for 16 locations around the globe with respect to their net energy yield, N and P recovery, CO_2 emission and area requirements. The results were compared with the CAS system. Both configurations are based on combined bioflocculation and anaerobic digestion but with different nutrient removal technologies, i.e. partial nitritation/Anammox or microalgae treatment. The results quantitatively support the pre-assumption that the applicability of the two configurations are strongly location dependent. The configuration with (cold) partial nitritation/Anammox is applicable in tropical regions and some locations in temperate regions, such as Southern Europe and Southern part of South America. The configuration with microalgae treatment is only applicable the whole year round in tropical regions that are close to the equator line, such as Southeastern Asia and Northern part of South America. On the locations with very low sewage temperatures, e.g. temperatures below 10°C, for example in Northern America and Eastern Europe, CAS systems are the only option. A sensitivity analysis of the configuration employing microalgae treatment shows that microalgal biomass yield and nutrient concentrations in the sewage have a critical impact on the area requirement and effluent concentrations.

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Chapter 4

Volatile fatty acids production from sewage organic matter by combined bioflocculation and anaerobic fermentation

Abstract

This work aims at exploring the feasibility of a combined process bioflocculation to concentrate sewage organic matter and anaerobic fermentation to produce volatile fatty acids (VFA). Bioflocculation, using a high-loaded aerobic membrane bioreactor (HL-MBR), was operated at an HRT of 1 hour and an SRT of 1 day. The HL-MBR process removed on average 83% of sewage COD, while only 10% of nitrogen and phosphorus was removed. During anaerobic fermentation of HL-MBR concentrate at an SRT of 5 days and 35°C, specific VFA production rate of 282 mg VFA-COD/g VSS could be reached and consisted of 50% acetate, 40% propionate and 10% butyrate. More than 75% of sewage COD was diverted to the concentrate, but only 15% sewage COD was recovered as VFA, due to incomplete VSS degradation at the short treatment time applied. This shows that combined process for the VFA production is technologically feasible and needs further optimization.

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4.1 Introduction

Conventional (aerobic) municipal wastewater treatment plants are designed to remove organic matter and nutrients such that an effluent quality is produced that meets the discharge guidelines. Instead of a waste, municipal wastewater recently has started to be considered a valuable resource in terms of reusable water, energy and nutrients (Stowa, 2010; Wang et al., 2012). Unfortunately, generally the concentration of organic matter in sewage is low and sewage has a relatively low temperature of e.g. 10–20°C (Metcalf and Eddy, 2004). These characteristics prevent the direct production of valuable resources from organic matter, such as methane or volatile fatty acids (VFA), and makes pre-treatment to concentrate the organic matter necessary. Aerobic bioflocculation of raw sewage in a high-loaded membrane bioreactor (HL-MBR) is a promising technique to accomplish such a concentration step, while at the same time it can produce a water quality that is fit for reuse (Akanyeti et al., 2010; Faust et al., 2014).

Often anaerobic digestion is applied to reduce the amount of primary sludge (PS) and secondary activated sludge (AS) and to produce methane from these solids (Lettinga, 1995). This process consists of four subsequent steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Complete digestion results in the production of methane, whereas the first three steps have VFA as the main end product. Production of VFA is useful, as they are the starting compounds for subsequent production of a wide range of higher value products, such as hydrogen gas, medium-chain fatty acids and bioplastics. The VFA can also be used to enhance biological nutrient removal (Lee et al., 2014). However, to produce VFA, methanogenesis should be avoided. This can be accomplished by applying a short solids (sludge) retention time (SRT) to wash-out the methanogenic microorganisms and/or by operating the anaerobic reactors at extreme pH values. For example, no detectable methane production was found in anaerobic fermenters operated at extremely low pH (pH 4) or extremely high pH (pH 10–11) (Chen et al., 2007; Yu et al., 2013; Yuan et al., 2006).

Previous studies on solids hydrolysis and VFA production from sewage organic matter were conducted with PS, AS, or a mixture of these. The higher fraction of biodegradable organic matter in PS gives a higher VFA yield per gram of solids compared to AS or a mixture of PS and AS (Ucisik and Henze, 2008; Yuan et al., 2009). Ucisik and Henze (2008) reported a specific

VFA production of 270 mg chemical oxygen demand (COD) per gram of volatile suspended solids (VSS) from PS and this VFA was composed of 50% acetate, 35% propionate, 10% butyrate, and 5% other VFA. This result is in line with the study by Ferreiro and Soto (2003), who found a specific VFA production of 170–370 mg COD/g VSS of PS and a VFA composition of 37–60% acetate, 30–55% propionate and 8–20% butyrate.

Akanyeti et al. (2010) reported that with a combination of aerobic bioflocculation and subsequent anaerobic digestion at least 35% of sewage COD can be converted to methane. This yield is much higher than a methane recovery of 18% when PS and/or a mixture of PS and AS are digested (Cao, 2011). This is because the bioflocculation process not only concentrates the COD that is contained in the settleable solids, but also all of the suspended COD, colloidal COD and even part of the soluble COD. Besides, with bioflocculation aerobic mineralization of organic matter, taking place in conventional activated sludge (CAS) systems, is largely avoided. For example, Faust et al. (2014) showed that, given proper operational conditions, excellent bioflocculation is possible, as only 10–15% of the COD load is lost by mineralization. Model calculations by Khiewwijit et al. (2015) also showed a high potential COD recovery. However, the model calculations focussed on methane production rather than on the production of more valuable VFA.

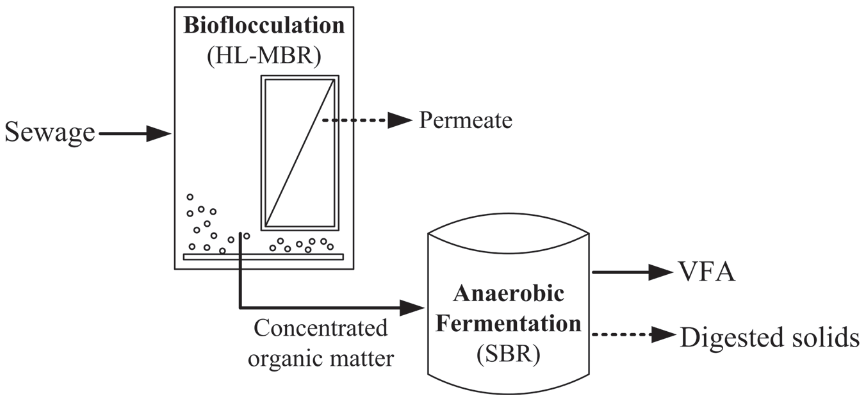

Figure 4.1: Combined bioflocculation using a high-loaded MBR (HL-MBR) to concentrate sewage organic matter, and anaerobic fermentation using sequencing batch reactor (SBR) to produce VFA

In the literature no information is available about the COD recovery that can be achieved by combined bioflocculation and VFA production. Therefore, in this study the performance of this combination was further investigated (Figure 4.1), focusing on solids degradation, VFA production, VFA composition, and nitrogen (N) and phosphorus (P) release. For this purpose an HL-MBR was used for the bioflocculation process and an anaerobic sequencing batch reactor (SBR) for subsequent VFA production from the concentrate that was produced by the HL-MBR.

4.2 Materials and Methods

4.2.1 Municipal wastewater characteristics

Municipal wastewater was collected from a school and a few households nearby this school (Van Hall School Leeuwarden, The Netherlands). The wastewater first passed a sedimentation column to remove heavy inert particles like sand and was stored in a stirred buffer tank.

Table 4.1 gives a summary of the most important characteristics of the wastewater that was collected in the buffer tank. Occasional comparison of these characteristics with those of the raw wastewater confirmed that no significant changes in total COD, NH_4-N and PO_4-P took place in the sedimentation column. In the column less than 3% of the suspended COD was removed.

Table 4.1: Average characteristics of municipal wastewater fed to HL-MBR process (Concentrations are average values calculated from 56 grab samples taken over a period of 195 days. Standard deviations are shown between brackets.)

Analysis	Unit	Average value
Total COD	mg COD/L	310 (113)
Suspended COD	mg COD/L	162 (88)
Colloidal COD	mg COD/L	64 (49)
Soluble COD, SCOD	mg COD/L	84 (40)
NH_4-N	mg N/L	34 (13)
PO_4-P	mg P/L	5 (2)

4.2.2 HL-MBR bioflocculation

The HL-MBR was operated at a hydraulic retention time (HRT) of 1.0 ± 0.1 hours and an SRT of 1.0 ± 0.1 days to optimize flocculation and at the same time to minimize (aerobic) organic matter mineralization. The reactor design was the same as used by Faust et al. (2014) and by Akanyeti et al. (2010). The working volume of the reactor was 2.6 L and the reactor was equipped with two submerged flat sheet membranes (Kubota Corporation, UK). The chlorinated polyethylene membrane sheets had a surface area of 0.124 m^2 and an average nominal pore-size of 0.2 μm. Aeration and mixing were accomplished by pressurized air to maintain the minimum dissolved oxygen (DO) concentration of 2 mg O_2/L. This was checked with an online oxygen sensor (Oxymax COS22D, Endress+Hauser). Peristaltic pumps (Masterflex L/S, Cole-Parmer) were used to feed the wastewater and for permeate and concentrate production. To reduce membrane fouling the permeate pump was operated in cycles of 15 minutes permeation followed by 5 minutes relaxation. The concentrate pump was operated in cycles of 1 minute concentrate production, followed by 59 minutes relaxation. A PVC pipe of 3.5 cm diameter and 30 cm height was used to control the liquid level in the reactor. The membranes were cleaned mechanically by milli-Q water spraying at least once a day in order to remove a gel layer that was formed on the membrane surface during filtration.

4.2.3 Fermentation of HL-MBR concentrate

Approximately 400 mL sludge (19 g VSS/L) from an anaerobic digester treating a mixture of PS and AS (wastewater treatment plant of Ede, The Netherlands) was used to inoculate the fermenter. Every morning and evening HL-MBR concentrate was collected and stored at 4°C for a maximum of 7 days. The anaerobic fermenter was fed with this concentrate at a concentration of approximately 10 g total COD/L. This was accomplished by letting the HL-MBR concentrate settle and decanting part of the supernatant.

The SBR reactors were constructed of plexiglass, had a working volume of 4.0 L, and were equipped with a glass stirrer for mixing at a speed of 150–200 rpm. The pH was monitored with an online pH electrode (Orbisint CPS11D, Endress+Hauser). Strict anaerobic conditions were maintained by flushing with N_2 gas. The reactors were controlled at a temperature of 35 ± 1°C with a water bath. During a preliminary run and during the first two SBR cycles the SRT was set at 10 days. However, a relatively high methane production was observed and therefore the next four cycles a shorter SRT of 5 days was applied to accomplish wash-out of methanogenic biomass. In each cycle the HL-MBR concentrate was replaced and mixed with the mixed liquid solids at the end of a previous cycle. Table 4.2 summarizes the operational parameters.

Table 4.2: Operational SBR parameters for VFA production from the HL-MBR concentrate

Cycle	SRT (days)	Solids replacement after a cycle end (%)	Cycle time (days)
Preliminary run	10	90[a]	9
1–2	10	90	9
3–6	5	95	5

[a] Inocolum seed sludge was taken from an anaerobic digester in wastewater treatment plant of Ede, The Netherlands.

4.2.4 Analytical methods

Mixed liquor samples were taken at least twice a week from the wastewater influent of the HL-MBR process, from the HL-MBR permeate, and from the concentrate. Total COD, paper filtered COD (Whatman, 589/1) and 0.45 μm membrane filtered COD were analyzed with a Dr. Hach Lange cuvette. Suspended COD was calculated as the difference between total COD and paper filtered COD, colloidal COD was considered as the difference between paper filtered and 0.45 μm membrane filtered COD, and 0.45 μm membrane filtered COD was the soluble COD (SCOD). From the 0.45 μm membrane filtered samples, NH_4-N was analyzed with a Dr. Hach Lange cuvette and anions concentrations (PO_4^{3-}, NO_2^-, and NO_3^-) were determined using an Ion chromatography device (Metrohm Compact IC 761, Switzerland), equipped with a conductivity detector, column Metrohm Metrosep A Supp 5, 150/4.0 mm, pre-column Metrohm Metrosep A Supp 4/5 Guard, and auto sampler (Spark Triathlon). Mixed liquor suspended solids (MLSS) as total suspended solids (TSS) and mixed liquor volatile suspended solids (MLVSS) as VSS were measured according to standard methods (APHA, 1998).

In the anaerobic fermenters the gas was collected through a rubber septum using a pressure-lock glass syringe 1 mL (VICI Precision Sampling, Pressure-Lok® Precision Analytical Syringe, USA) and analyzed for H_2, O_2, N_2, CH_4, CO_2, and H_2S by a micro gas chromatography (µGC, Varian CP 4900, USA), equipped with a thermal conductivity detector and two columns: a Mol Sieve 5A PLOT 10m x 0.53 mm column at 80°C (column 1) using argon as carrier gas and PoraPlot U-10m column at 65°C (column 2) using helium as carrier gas. The gas injection volume was 1 mL with a flow gas of 1.47 mL/min and a running time of 90 seconds.

Mixed liquor samples from the fermenters were first centrifuged at 14,000 rpm for 10 minutes under room temperature and then filtered with a 0.45 µm membrane filter. Total COD concentration was analyzed using the mixed liquid sample with a Dr. Hach Lange cuvette. Soluble COD, NH_4-N and PO_4-P concentrations of samples were analyzed as described previously.

To measure the VFA concentrations of acetate (C2), propionate (C3), and butyrate (C4), the filtrated sample was analyzed by an Ion Chromatography device (IC) (Metrohm Compact IC 761, Switzerland), equipped with a conductivity detector, column Phenomenex Synergi 4u hydro-RP 80A, pre-column Metrosep Organic Acids Guard. IC methods can be used to separate VFA with linear carbon chains of up to four carbon atoms in length. During the separation step, each acid interacts differently with respect to the chosen stationary phase. In our case, the stationary phase consists of silicagel as a carrier material with chemically bonded alkyl groups containing 18 carbon atoms. Sulphuric acid (0.5 mM) is used as the mobile phase, which causes the acids to become non-dissociated. After separation, a chemical suppressor (Metrohm Suppressor, Switzerland) with an eluent of 50 mM lithium carbonate is used to dissociate VFA and form CO_2. Acid anions travel through the chemical suppressor along with the mobile phase. The suppressors are equipped with conductivity detectors to suppress the conductivity of mobile phase, while increasing the peak response of each acid anion. The VFA concentration was converted to COD concentration by using the following conversion factors: 1.07 g COD/g acetate, 1.51 g COD/g propionate, and 1.82 g COD/g butyrate. Total VFA was calculated as the sum of all the individual VFA. A specific VFA production was calculated by subtracting the VFA concentration in the feed HL-MBR concentrate from the VFA production at the end of each cycle and expressed as the mass of VFA-COD per unit mass of VSS in the feed concentrate (mg VFA-COD/g VSS_{feed}). Solubilization was expressed as the percentage mass ratio of soluble COD to the total COD in the feed concentrate. The NH_4-N and PO_4-P releases were expressed per unit mass of VSS degraded (mg NH_4-N/g $VSS_{degraded}$ and mg PO_4-P/g $VSS_{degraded}$).

4.3 Results and Discussion

4.3.1 Performance of bioflocculation in HL-MBR

4.3.1.1 COD mass balance of HL-MBR

Figure 4.2 shows the average COD mass balance for the HL-MBR bioflocculation process during its 195 days of operation. Removal of total COD was 83%, giving an average permeate concentration of 49 ± 14 mg COD/L. This shows that in spite of the extremely short HRT (1 hour) and SRT (1 day) that were applied, the HL-MBR process can achieve an effluent COD concentration that easily meets the EU discharge guideline of 125 mg COD/L (Council Directive, 1991). This result is in agreement with Akanyeti et al. (2010), who reported a COD removal efficiency of 77–87% at SRTs of 0.25–1 day and a permeate COD concentration of 64–76 mg COD/L.

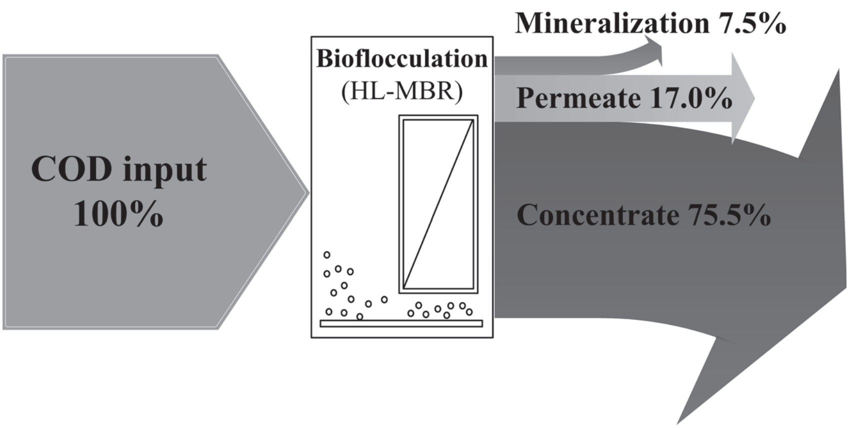

Figure 4.2: Average COD mass balance for the HL-MBR bioflocculation process during 195 days of operation

In this study, more than 75% of the sewage COD ended up in the concentrate. This recovery is very high compared to CAS systems, where approximately 40–60% of the sewage COD ends up as PS and AS. Aerobic mineralization was calculated as the closure of the COD mass balance and was only 7.5%.

4.3.1.2 Composition of HL-MBR concentrate

Table 4.3 shows the average composition of the HL-MBR concentrate. These results indicate an effective bioflocculation process: in the sewage approximately 50% of the total COD consisted of suspended matter (Table 4.1), whereas in the concentrate of the HL-MBR this was more than 90%.

Table 4.3: Characteristics of the HL-MBR waste concentrate fed to the anaerobic SBR reactors (pH and concentrations are average values, and standard deviations are shown between brackets.)

Analysis	1^{st} and 2^{nd}cycles	3^{rd} and 4^{th} cycles	5^{th} and 6^{th} cycles
pH	7.0 (0.1)	7.0 (0.1)	7.1 (0.1)
VSS (g/L)	6.7 (0.4)	7.0 (0.3)	6.6 (0.2)
TSS (g/L)	7.9 (0.4)	8.0 (0.1)	7.9 (0.3)
Total COD (mg/L)	10559 (561)	10427 (200)	10282 (166)
Suspended COD (mg/L)	10004 (212)	9393 (199)	9475 (205)
Colloidal COD (mg/L)	186 (11)	300 (25)	190 (18)
Soluble COD (mg/L)	370 (153)	735 (26)	617 (57)
NH_4-N (mg/L)	55 (19)	55 (5)	36 (7)
PO_4-P (mg/L)	22 (5)	26 (1)	20 (1)
VFA (mg VFA-COD/L)	124 (65)	496 (31)	449 (29)

Higher concentrations of NH_4-N, PO_4-P, and VFA were observed after storage at 4°C than in fresh concentrate. Apparently hydrolysis and acidification continued even at 4°C. However, storage only had a minor effect on the overall process performance compared to hydrolysis and acidification taking place in the anaerobic fermenters as will be further explained below.

4.3.2 Performance of anaerobic fermenters

4.3.2.1 VSS degradation and nitrogen and phosphorus release

Figure 4.3 shows the VSS concentration during the SBR cycles. During the first two cycles, i.e. at an SRT of 10 days, 51% of the VSS was degraded. This is somewhat higher than what was found for PS fermentation. Ferreiro and Soto (2003) reported a VSS degradation of 36–46% for PS. However, it is unclear at the moment whether this 51% VSS degraded would be a maximum value for the HL-MBR concentrate fermentation. In the literature, information about the solids degradation of PS and the HL-MBR concentrate through fermentation is still limited and needs to be further investigated. Moreover, because a considerable amount of COD was converted to methane (0.11 g CH_4-COD/g total COD_{feed}), it was decided to shorten the SRT to 5 days to accomplish wash-out of the methanogens. This indeed resulted in a much lower average methane production of 0.03 g CH_4-COD/g total COD_{feed}. The methane production rate at an SRT of 10 days was 69 mL CH_4/L HL-MBR concentrate/day, while it was only 24 mL CH_4/L HL-MBR concentrate/day at an SRT of 5 days. However, as a result of the shorter treatment time the average efficiency of VSS degradation decreased from 51% to 35% with an SRT of 5 days.

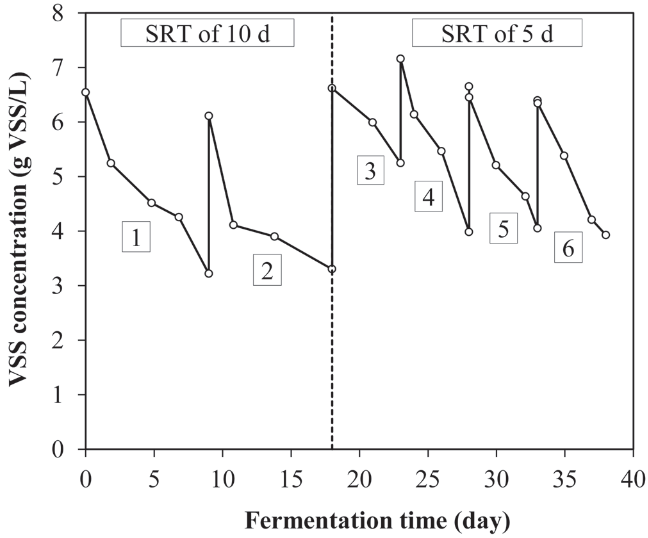

Figure 4.3: VSS concentration during fermentation of HL-MBR concentrate

Degradation of VSS was accompanied by a release of NH_4-N and PO_4-P of 64 mg NH_4-N/g $VSS_{degraded}$ and 23 mg PO_4-P/g $VSS_{degraded}$, respectively. Both PO_4-P and NH_4-N release seem to be reasonable considering typical nitrogen and phosphorus content of municipal wastewater solids (Henze et al., 2008) and also comparable with the measured values of total nitrogen and total phosphorus in the mixed liquid solids of the HL-MBR concentrate (data not shown).

4.3.2.2 COD solubilization and VFA production

Figure 4.4 shows the solubilization of COD and concomitant VFA production. Mainly due to the occurrence of methanogenesis in the first two cycles, the average concentrations of soluble COD and VFA both were relatively low. At an SRT of 10 days, soluble COD levels reached an average value of only 15% of the 10 g COD/L HL-MBR concentrate. The VFA production was limited to an average of 645 mg VFA-COD/L and methane formed was 11% of the concentrate COD input.

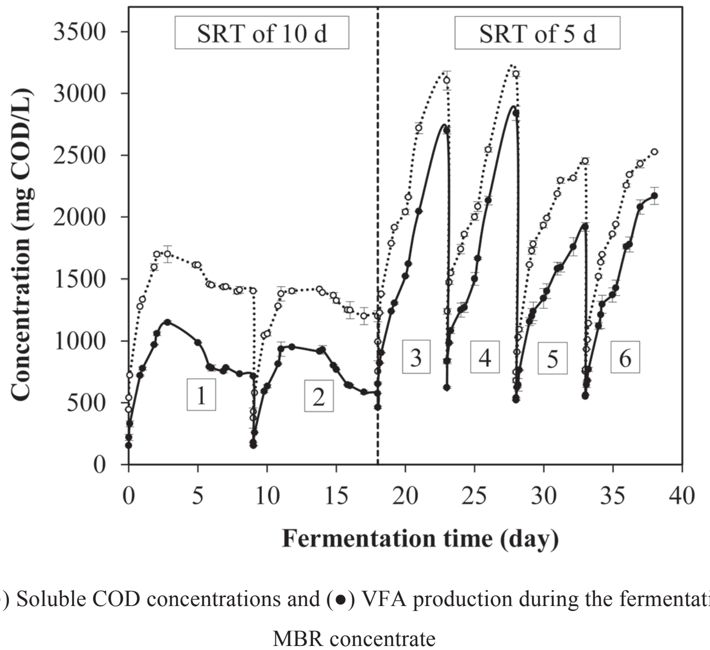

Figure 4.4: (○) Soluble COD concentrations and (●) VFA production during the fermentation of the HL-MBR concentrate

Upon changing an SRT to 5 days in cycles 3–6, soluble COD levels increased to an average of 27% and the production of VFA increased to an average of 2407 mg VFA-COD/L, whereas methane production reduced to 3% of the concentrate COD input. These results demonstrate that the reduction in the SRT leads to higher soluble COD levels, reduced loss to methane and increased the recovery of VFA. The results obtained at an SRT of 5 days correspond to an average specific VFA production of 282 ± 51 mg VFA-COD/g VSS_{feed} or 0.9 g VFA-COD/g $VSS_{degraded}$. A similar result of 270 mg VFA-COD/g VSS was reported for PS fermentation by Ucisik and Henze (2008). Ferreiro and Soto (2003) showed a VFA formation of 0.35–1.31 g VFA-COD/g $VSS_{degraded}$ for PS fermentation, which increased when the temperature increased and initial VSS concentration decreased. Thus, the result of 0.9 g VFA-COD/g $VSS_{degraded}$ in this study is relatively high compared to the PS fermentation under similar conditions, i.e. nearly 0.5 g VFA-COD/g $VSS_{degraded}$ at a temperature of 35°C and 5.7 g VSS of PS/L. This higher yield may be caused by a larger biodegradable organic fraction in the HL-MBR concentrate compared to PS, where the COD is mainly associated with the settleable solids.

4.3.2.3 VFA composition

The VFA were composed of 50% acetate, 40% propionate and 10% butyrate. However, it is important to note that this VFA composition is related to the range in municipal wastewater characteristics, as presented in Table 4.1. For example, total COD, NH_4-N and PO_4-P concentrations were in the range between 197 and 423 mg COD/L, 21 and 47 mg N/L and 3 and 7 mg P/L, respectively. This is in line with results obtained by Ferreiro and Soto (2003), who reported that the production of VFA from PS at a temperature of 35°C mainly consisted of acetate (60%), while propionate and butyrate accounted for about 30% and 10%, respectively. Similarly, Ucisik and Henze (2008) reported that PS fermentation gave 50% acetate, 35% propionate, 10% butyrate, and 5% other VFA. The consequence of this finding for H_2 or bioplastic production from these VFA is still largely unknown, because the quality of bioplastics, for example, is dependent on the VFA composition and the presence of organic compounds other than VFA (Dias et al., 2006).

4.3.3 Overall COD, N, and P mass balances

Figure 4.5 shows the average COD, N and P mass balances of the overall process. An average of 15% of the sewage COD was converted to VFA (C2–C4). This is comparable to a COD recovery as methane when anaerobic digestion is applied for the PS and AS produced by CAS systems (Cao, 2011). However, it is far below the expected recovery of 35–40% based on a previous study by Akanyeti et al. (2010). Comparing VSS degradation at SRTs of 5 days and 10 days of 35% and 51%, respectively, show that VFA production at an SRT of 5 days was limited by the extent of VSS reduction (Figure 4.3 and Figure 4.4). Thus, longer treatment times are required to improve VFA production. More VSS degradation would also considerably reduce the amount of waste solids from anaerobic digester to about 20% of the sewage COD (Khiewwijit et al., 2015; Cao, 2011), which with 58.5% (Figure 4.5) was still very high. However, it was also demonstrated that at an SRT of 10 days methanogenesis cannot be avoided.

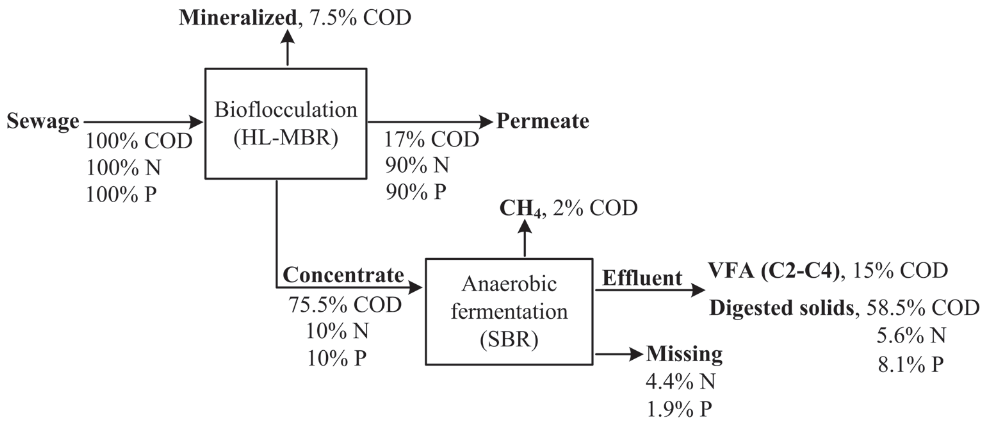

Figure 4.5: Average COD, NH_4-N and PO_4-P mass balances of the combined process of HL-MBR bioflocculation and anaerobic VFA production

To be able to prolong the SRT while still avoiding methanogenesis, extreme pH levels could be applied. Assuming that at least 51% VSS degradation is possible, the application of extreme pH levels may further increase the VFA recovery to at least 24% of the sewage COD. However, it is unclear whether at an SRT longer than 5 days this will still result in the similar VSS reduction. In particular, a high pH could be interesting. Previous studies reported that COD solubilization increased at acidic (pH 5) and alkaline (pH 9, 10, 11) conditions for AS and a mixture of AS and PS fermentation (Chen et al., 2007; Maspolim et al., 2015). However, higher VFA recovery was observed at pH of 8–10 for a mixture of AS and PS fermentation (Maspolim et al., 2015) and at pH of 9–11 for AS fermentation (Chen et al., 2007; Jie et al., 2014) as compare to acidic and neutral conditions. For example, Jie et al. (2014) found a specific VFA production of 300 mg VFA-COD/g VSS during AS fermentation at pH 10, whereas at a pH of 5 the specific production only was 80 mg VFA-COD/g VSS. Similarly, Yuan et al. (2006) showed that VFA production at pH 10 was more than three times higher than at pH 5.

Microbial production of VFA is subject to production inhibition and therefore the formed VFA products should preferably be extracted from the fermenter during production (Siegert and Banks, 2005). Several VFA extraction technologies have been investigated such as ion-exchange, adsorption, precipitation, nanofiltration, reverse osmosis, and electrodialysis (ED) (López-Garzón and Straathof, 2014). Especially, ED in combination with high pH offers an interesting potential. VFA that are generated under an alkaline pH are in the anionic form and can be directly extracted from the fermentation broth using ED (Huang et al., 2007; Vertova et al., 2009). Meanwhile, it should also be noted that alkaline pH may affect the VFA composition of the end product and may cause toxicity to the fermenting microorganisms by free ammonia. However, even in case all VSS available in the HL-MBR concentrate would be degraded and therefore ammonia would be released at maximum levels of about 500 mg NH_3-N/L, this value will still be far below the toxicity levels of NH_3-N for hydrolysis as found by Fernandes et al. (2012). Therefore, ammonia inhibition is not expected to become a limiting factor in VFA recovery at high pH.

Another option to improve VSS degradation while avoiding methanogenesis would be to apply well known pre-treatment technologies, such as thermal, alkaline and microwave treatment (Lee et al., 2014). In particular, an alkaline pre-treatment method is interesting because of its high efficiency, simplicity and convenient operation. Feng et al. (2013) showed that the methane production after pre-treatment at a pH of 10 during 4 hours was more than 1.5 times than methane production from untreated AS.

Figure 4.5 also shows that approximately 90% of N (NH_4-N) and P (PO_4-P) in the sewage were conserved in the permeate of the HL-MBR bioflocculation reactor. This makes the permeate ideal for irrigation, because the HL-MBR permeate is free from solids and pathogens. If an application as irrigation water is not anticipated, phosphate may be recovered from the HL-MBR permeate, for instance by struvite precipitation. The remaining N can then be removed by a cold Anammox process, which is currently being developed (e.g. Hendrickx et al., 2012).

4.4 Conclusions

A combined bioflocculation and fermentation process was investigated with the aim to achieve a more efficient COD recovery as VFA compared to methane-COD recovery produced from a conventional anaerobic digestion for PS and AS. Bioflocculation in HL-MBR shows efficient COD recovery from sewage, as approximately 75% was diverted to the concentrate. A specific VFA production of 282 mg VFA-COD/g VSS_{feed} composed of 50% acetate, 40% propionate and 10% butyrate was obtained. This combined process for the VFA production is technologically feasible. Methane production was inhibited at an SRT of 5 days, but incomplete VSS degradation mainly limited the VFA production.

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Chapter 5

Production of volatile fatty acids from sewage organic matter by combined bioflocculation and alkaline fermentation

Abstract

This study explored the potential of volatile fatty acids (VFA) production from sewage by a combined high-loaded membrane bioreactor and sequencing batch fermenter. VFA production was optimized with respect to SRT and alkaline pH (pH 8–10). Application of pH shock to a value of 9 at the start of a sequencing batch cycle, followed by a pH uncontrolled phase for 7 days, gave the highest VFA yield of 440 mg VFA-COD/g VSS. This yield was much higher than at fermentation without pH control or at a constant pH between 8 and 10. The high yield in the pH 9 shocked system could be explained by (1) a reduction of methanogenic activity, or (2) a high degree of solids degradation or (3) an enhanced protein hydrolysis and fermentation. VFA production can be further optimized by fine-tuning pH level and longer operation, possibly allowing enrichment of alkaliphilic and alkali-tolerant fermenting microorganisms.

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5.1 Introduction

Anaerobic fermentation of sewage organic matter to volatile fatty acids (VFA) presents a promising alternative for methane production from primary sludge (PS) and/or excess (secondary) activated sludge (AS) generated by conventional activated sludge (CAS) systems (Lee et al., 2014). VFA are preferred over methane as an end product, because these can be the starting compounds for the production of a wide range of higher value products, such as bioplastics (polyhydroxyalkanoates) (Morgan-Sagastume et al., 2014), lipids for biodiesel (Fei et al., 2011) and medium-chain fatty acids (Grootscholten et al., 2014). Unfortunately, CAS systems employ intensive and energy consuming aerobic mineralization, which largely destroys sewage organic matter by biodegradation leading to mineralization. To keep wastewater organics available for producing high value products, a new concept was developed to consolidate sewage COD (chemical oxygen demand) (Akanyeti et al., 2010; Faust et al., 2014a; Faust et al., 2014b; Khiewwijit et al., 2015b) and to optimize the subsequent VFA production from this concentrated COD (Khiewwijit et al., 2015a).

In this concept, sewage COD is first concentrated by bioflocculation in a high-loaded membrane bioreactor (HL-MBR). A much higher VFA yield can be expected from the bioflocculated concentrate compared to PS and AS, because the concentrate contains more than 75% of the sewage COD, including all settleable solids, suspended COD, colloidal COD and consolidates even part of the soluble COD (Faust et al., 2014a; Faust et al., 2014b; Khiewwijit et al., 2015a). Besides, in this manner aerobic mineralization of biodegradable COD is largely avoided. When all of the concentrated COD would be converted into methane, a recovery of 35–40% of the sewage COD is feasible, which is at least two times the methane yield obtained in CAS systems (Akanyeti et al., 2010; Cao, 2011; Khiewwijit et al., 2015b). Therefore, a similar VFA recovery ratio on COD basis can be anticipated using the combination of bioflocculation and VFA fermentation. Khiewwijit et al. (2015a) studied VFA production from 10 g COD/L bioflocculated concentrate in anaerobic sequencing batch reactor (SBR). In these experiments the pH during fermentation was not controlled, and during fermentation decreased from 7.1 to typically 4.9–5.5 at a solids (sludge) retention time (SRT) of 5 days. The technological feasibility of the HL-MBR and anaerobic fermentation combination was demonstrated, but the VFA production yield was only 15% of the sewage COD. The main reasons for this low production were different in the two different SRT systems used. Methanogenesis could not be avoided at an SRT of 10 days, and a large fraction of the VFA was subsequently converted into methane. At a short SRT of 5 days, methane production could be prevented, but solubilization of the bioflocculated sewage solids was relatively low: 35% compared to 51% at an SRT of 10 days.

To improve the VFA yield, alkaline pH fermentation was considered to overcome these two problems. The impact of a high pH on fermentation of sewage solids has recently been explored with PS and AS. For example, Chen et al. (2007) and Yu et al. (2008) showed that at pH 10–11 methanogenesis was inhibited. This inhibition contributed to a significantly higher VFA production than at lower pH values. Chen et al. (2007) also showed that VFA production from AS at a pH of 10 was more than 6 times higher than at a pH of 4. Similar results were found by Liu et al. (2012), who reported inhibition of methanogens at pH 3, 11 and 12, with a VFA yield at pH of 9 that was almost 10 times higher than at a pH of 3. Another advantage of a high pH may be the promotion of homoacetogenesis, i.e. the formation of acetate from inorganic carbon and H_2, as observed by Modestra et al. (2015). The promotion of homoacetogenesis would also certainly contribute to a higher VFA yield. Finally, with alkaline conditions during fermentation the VFA are present as anions. This can facilitate extraction of a high quality VFA product by electrochemical techniques, and creates the possibility to combine this type of extraction with electrochemical alkalinity production necessary to maintain a high pH level (Huang et al., 2007).

In addition to the occurrence of methanogenesis, a limited solubilization of sewage solids can also be a bottleneck for VFA production (Eastman and Ferguson, 1981; Khiewwijit et al., 2015a). To enhance the solubilization process, typically pre-treatment is applied, including thermal and mechanical methods, microwave, ultrasound exposure, acid/base addition, or combinations of these, such as the thermo-pressure hydrolysis (TDH) (Carlsson et al., 2012; Lee et al., 2014). Of these methods, TDH probably is the most widely applied (Phothilangka et al., 2008). However, it also is a relatively expensive technique with a high energy demand required to generate the high pressure (19–21 bars) and temperature (typically 180°C). Alkaline pre-treatment enhances solids degradation. It disrupts the floc structure and microbial cell walls, and in this manner more biopolymers such as proteins, carbohydrates and lipids become available for subsequent hydrolysis, acid fermentation and methanogenesis. For example, Feng et al. (2013) showed that methane production from AS after alkaline pre-treatment of 4 hours at a pH of 10 was almost two times of that without pre-treatment. Similarly, Kim et al. (2010) showed that solids degradation in a mixture of AS and PS increased by a factor of 2.7 after alkaline pre-treatment of 1 hour at a pH of 13.

All of the studies mentioned above used PS and AS from CAS systems. VFA production from bioflocculated sewage organic matter under alkaline conditions has not yet been studied. Therefore, in this study, a combined bioflocculation and alkaline VFA production process was investigated at several pH values (8–10). The results were compared to a fermentation process without pH control with respect to solids degradation, VFA production and VFA composition. In addition, fermenter operation at a constant pH was compared with the application of short pH shocks to limit methanogenic activity and to enhance biosolids hydrolysis, in order to further optimize VFA production.

5.2 Materials and Methods

5.2.1 Fermentation conditions of HL-MBR concentrate

Two 4.0 L plexiglass reactors were equipped with a glass stirrer for mixing at 150–200 rpm. The pH was monitored with an online pH electrode (Orbisint CPS11D, Endress+Hauser). Strict anaerobic conditions were maintained by flushing with N_2 gas. The reactors were controlled at a temperature of 35 ± 1°C with a water bath. The pH was automatically controlled by a liquid dosing pump (SIMDOS 10, KNF Benelux Netherlands) at pH values of 8, 9 or 10 using 2 M hydroxide solution (1 M sodium hydroxide and 1 M potassium hydroxide).

Using the same reactors preliminary sequencing batch runs were carried out for 38 days and with HL-MBR concentrate as their feed at pH 10 (data not shown) and without pH control (Khiewwijit et al., 2015a). For this purpose both reactors were inoculated with 400 mL sludge (19 g VSS/L) from an anaerobic digester treating a mixture of PS and AS (wastewater treatment plant of Ede, The Netherlands). In subsequent reactor runs, which will be described in this paper, a mixture of 200 mL of the solids from the reactor that was operated at pH 10 and 200 mL of the solids from the reactor without pH control was taken as the inoculum.

SBR operation was carried out in three sequential stages. Table 5.1 summarizes the operational conditions of the sequencing batch fermenter that were applied. During these stages, after each sequencing batch cycle a fixed volume of the (mixed) reactor contents was replaced by the same volume of HL-MBR concentrate.

Table 5.1: Sequencing batch fermenter operation to produce VFA from HL-MBR concentrate

Stages/Cycles	pH Reactor 1	pH Reactor 2	SRT (days)	Solids replacement after a cycle end (%)	Cycle time (days)	pH maintained
Preliminary run	9	10	10	90[a]	9	Full cycle
Stage I/1–2	9	10	10	90	9	Full cycle
Stage II/3–4	9	8	5	95[b]	5	Full cycle
Stage III/5–6	9	10	5	95[c]	5	Shock of 3.5 h

[a] Inocolum seed sludge, taken from a mixture of mixed solids of a sequencing batch fermentation experiment at pH 10 and uncontrolled pH, operating for 38 days.
[b] In cycle 3 the mixed liquid solids were taken at the end of cycle 2 with pH 9.
[c] In cycle 5 the mixed liquid solids were taken at the end of cycle 2 with the same pH condition.

Six sequencing batch cycles were performed. Stage-I, consisting of two cycles, was carried out to test the hypothesis that high pH combined with a long SRT can improve the VFA yield. Both reactors were operated at an SRT of 10 days and the pH was controlled at 9 or 10. Because a relatively low VFA production was observed in stage-I, which will be explained later on, during the two cycles of stage-II the pH level in reactor 2 was reduced to 8. In addition, the SRT of both reactors was decreased from 10 to 5 days to promote wash-out of methanogens. In stage-III, the effect of a temporary shock increase in pH to a value of 9 or 10 of 3.5 hours was studied. After this shock, at the start of a sequencing batch cycle, the pH was not further controlled.

5.2.2 HL-MBR concentrate

The production of HL-MBR concentrate from sewage was described in detail by Khiewwijit et al. (2015a). The concentrate was stored at 4°C for a maximum period of 7 days. Table 5.2 gives the average composition of the HL-MBR concentrate that was used in this study. Compared to fresh HL-MBR concentrate, hydrolysis and acidification continued during storage at 4°C, which resulted in higher concentrations of VFA, ammonium (NH_4-N) and phosphate (PO_4-P). However, VFA production was negligible compared to hydrolysis and acidification during fermenter operation.

Table 5.2: Characteristics of HL-MBR concentrate fed to the anaerobic sequencing batch reactors

Analysis	1st and 2nd cycles	3rd and 4th cycles	5th and 6th cycles
pH	7.0 ± 0.1	7.1± 0.1	7.1 ± 0.2
VSS (g/L)	6.2 ± 0.5	6.4 ± 0.8	6.1 ± 0.3
TSS (g/L)	7.2 ± 0.6	7.6 ± 1.3	7.3 ± 0.9
Total COD (mg/L)	10819 ± 810	10508 ± 220	10305 ± 273
Suspended COD (mg/L)	10041 ± 718	9766 ± 72	9387 ± 143
Colloidal COD (mg/L)	182 ± 77	149 ± 48	204 ± 24
Soluble COD, SCOD (mg/L)	596 ± 15	593 ± 243	714 ± 392
NH_4-N (mg/L)	55 ± 1	42 ± 8	66 ± 27
PO_4-P (mg/L)	25 ± 2	21 ± 10	24 ± 18
VFA (mg VFA-COD/L)	326 ± 34	424 ± 235	481 ± 263

pH and concentrations are mean values.

5.2.3 Biological methane potential (BMP)

To determine the biological methane potential (BMP) of the soluble compounds, supernatant at the end of cycles 1–2 from the reactor operated at pH 10 was obtained by centrifugation. With this supernatant the BMP was determined using sludge from an anaerobic digester treating a mixture of PS and AS (wastewater treatment plant of Ede, The Netherlands). The test was carried out according to a method described in detail by Angelidaki et al. (2007).

5.2.4 Analytical methods

Mixed liquor solids samples from the anaerobic sequencing batch fermentation were first centrifuged at 14,000 rpm for 10 minutes and then filtered with a 0.45 μm membrane filter. Total COD concentration was analyzed using the mixed solids samples with a Dr. Hach Lange cuvette. The membrane filter samples were used to analyze the soluble COD, NH_4-N, PO_4-P, and VFA concentrations. Soluble COD, NH_4-N were analyzed using a Dr. Hach Lange cuvette. Gas compositions were analyzed using a micro gas chromatography (μGC, Varian CP 4900, USA). The measurements of PO_4-P and VFA (acetate, propionate and butyrate) were done with an ion chromatography device (Metrohm Compact IC 761, Switzerland), the same as described previously in the study of Khiewwijit et al. (2015a). Mixed liquor suspended solids (MLSS) as total suspended solids (TSS) and mixed liquor volatile suspended solids (MLVSS) as volatile suspended solids (VSS) were measured according to standard methods (APHA, 1998). The measurement of soluble proteins was determined using a bicinchoninic acid assay kit (Pierce™ BCA, Proteins Assay kit) and soluble polysaccharides was measured using the phenol-sulfuric acid method (Dubois et al., 1956).

The COD conversion factors for VFA are 1.07 g COD/g acetate, 1.51 g COD/g propionate and 1.82 g COD/g butyrate. The COD conversion factor for polysaccharides (carbohydrate) is 1.07 g COD/g glucose and for proteins (bovine serum albumin, BSA) it is 1.5 g COD/g BSA (Maspolim et al., 2015). Total VFA-COD concentration was calculated as the sum of the individual VFA. Specific VFA production or VFA yield was calculated by subtracting the VFA concentration in the feed HL-MBR concentrate from the VFA production at the end of each cycle and expressed in terms of VFA-COD per unit mass of VSS in the feed concentrate (mg VFA-COD/g VSS).

5.3 Results and Discussion

Table 5.3 summarizes the effects of SRT and pH control on VSS reduction, COD solubilization and VFA production during fermentation of HL-MBR concentrate, and the comparison of these results to those obtained by Khiewwijit et al. (2015a) for fermentation without pH control. SRT, constant pH control and the application of pH shocks all had a strong effect on solids degradation and VFA production, as will be described in more detail below.

5.3.1 Operation at controlled pH

5.3.1.1 VSS degradation

Figure 5.1 shows VSS concentrations during cycles 1–2 at pH 9 and 10, both at an SRT of 10 days and during cycles 3–4 at pH 9 and 8 at an SRT of 5 days. At an SRT of 10 days VSS degradation was higher at pH 10 (76 ± 4%) than at pH 9 (68 ± 5%), see Table 5.3. In both reactors methane production was insignificant, i.e. less than 0.7% of the 10 g/L of total COD that was fed to the reactors with the HL-MBR concentrate. This is in agreement with other studies, showing that methanogenic activity can be avoided if the pH is sufficiently high (Chen et al., 2007).

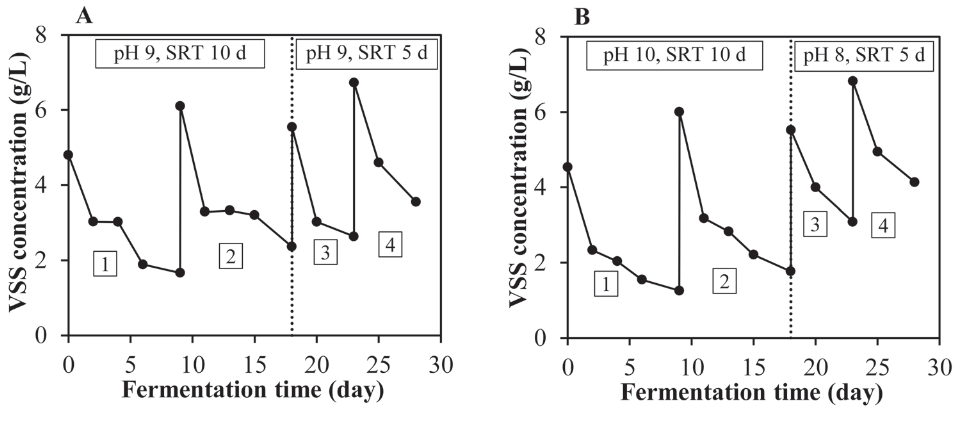

Figure 5.1: VSS concentration during fermentation of HL-MBR concentrate for sequencing batch cycles 1–4, (A) Reactor 1 and (B) Reactor 2 (Numbers in the box indicate the cycle.)

Table 5.3: Effect of SRT and pH conditions on VSS reduction, COD solubilization and VFA production from HL-MBR concentrate (Standard deviations were calculated from the results of two subsequent, identical sequencing batch cycles.)

Stages/Cycles	Reactor no.	Condition pH	Condition SRT (days)	VSS reduction (% of VSS_{feed})	COD solubilization (g $SCOD_{end}$/g total COD_{end})	VFA production (g VFA-COD_{end}/g total COD_{end})	Specific VFA production[c] (mg VFA-COD/g VSS)
Stage I/1–2	Reactor 1	9	10	68 ± 5	0.44 ± 0.05	0.23 ± 0.01	287 ± 11
	Reactor 2	10	10	76 ± 4	0.48 ± 0.07	0.20 ± 0.00	235 ± 2
Stage II/3–4	Reactor 1	9	5	52 ± 4	0.37 ± 0.03	0.22 ± 0.03	290 ± 1
	Reactor 2	8	5	44 ± 4	0.30 ± 0.00	0.21 ± 0.01	259 ± 33
Stage III/5–6	Reactor 1	Shock pH 9	5	54 ± 2	0.36 ± 0.06	0.25 ± 0.03	321 ± 46
	Reactor 2	Shock pH 10	5	52 ± 2	0.36 ± 0.07	0.22 ± 0.02	287 ± 30
Stage III/6	Reactor 1	Shock pH 9	7[a]	nd.	0.40	0.33	440
Previous study[b]		Uncontrolled	5	35	0.28	0.24	282

SCOD = soluble COD and nd. = data not determined.

Standard deviations are based on the concentration at the end of each cycle.

[a] The treatment time was prolonged to 7 days.

[b] Data taken from the study done by Khiewwijit et al. (2015a).

[c] Specific VFA production, or VFA yield, (mg VFA-COD/g VSS) = $\frac{VFA_{end}(mgCOD/L) - VFA_{HL\text{-}MBR,feed}(mgCOD/L)}{VSS_{HL\text{-}MBR,feed(g/L)}}$.

In cycles 3–4 the SRT of reactor 1 (Figure 5.1), operated at pH 9, was reduced from 10 to 5 days. This gave a reduction of VSS degradation from 68 ± 5% at an SRT of 10 days to 52 ± 4% at an SRT of 5 days. In reactor 2, which during cycles 3–4 was operated at pH 8 and an SRT of 5 days, VSS degradation was even lower (44 ± 4%). However, in all cases VSS degradation at these high pH levels was higher than the 35% obtained in earlier experiments without pH control (Table 5.3). At pH 8 methane production was 9% of the total COD of the HL-MBR concentrate, indicating that this pH was not high enough to avoid the occurrence of methanogenesis.

5.3.1.2 COD solubilization and VFA production

At an SRT of 10 days 44–48% of the total COD at the end of cycles 1–2 was present as soluble COD (Figure 5.2 and Table 5.3). As expected, at an SRT of 5 days and pH values of 9 and 8 this was considerably lower (37 ± 3% and 30 ± 0.3%, respectively), which matches with the lower VSS degradation under these conditions.

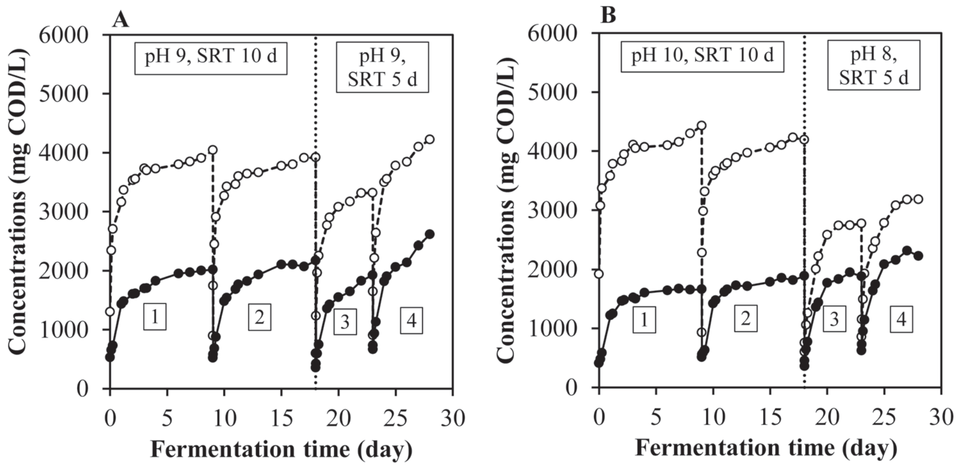

Figure 5.2: (○) Soluble COD concentrations and (●) VFA production during sequencing batch cycles 1–4 fermentation of HL-MBR concentrate, (A) Reactor 1 and (B) Reactor 2 (Numbers in the box indicate the cycle.)

Strikingly, even though large differences were observed in VSS degradation and COD solubilization, the specific VFA production yields were not that different: 287 ± 11 mg VFA-COD/g VSS at an SRT of 10 days and pH 9, 235 ± 2 mg VFA-COD/g VSS at an SRT of 10 days and pH 10, 290 ± 1 VFA-COD/g VSS at an SRT of 5 days and pH 9, and 259 ± 33 mg VFA-COD/g VSS at the same SRT but at pH 8. These production yields also are similar to the yield during HL-MBR concentrate fermentation without pH control of 282 mg VFA-COD/g VSS (Table 5.3). Also Maspolim et al. (2015) indicated that more VSS degradation or more COD solubilization at a high pH does not necessarily result in a higher VFA yield.

5.3.1.3 Gap between COD solubilization and VFA production

Interestingly, Figure 5.2 shows that the gap between soluble COD and VFA-COD at pH 8 was smaller than at pH 9 and 10, and in the reactor that was operated without pH control this gap was as small as 4% (Table 5.3). To investigate this in more detail, the concentration of soluble proteins and polysaccharides was measured in 0.45 µm membrane filtered samples at the end of cycles 1–2. This revealed that the gap between soluble COD and VFA at pH 9 consisted of 62 ± 7% proteins, 11 ± 0.8% polysaccharides and 27 ± 6% other unknown soluble compounds. Similarly, at pH 10 this gap consisted of 54 ± 5% proteins, 12 ± 0.2% polysaccharides and 34 ± 5% other soluble compounds. From this, it was concluded that at a high pH a considerable amount of (soluble) proteins was not converted to VFA. Apparently this counteracts the improved COD solubilization taking place at higher pH. A likely explanation is a suppressed proteolytic activity at pH 9–10 (Maspolim et al., 2015).

A BMP test was performed with supernatant that was collected at the end of cycles 1–2 from the pH 10 reactor, i.e. supernatant containing remaining soluble proteinaceous compounds. The supernatant was added to seed sludge sampled from a full-scale digester treating a mixture of AS and PS, because it can be assumed that this sludge contained a high proteolytic activity. The pH during the test was controlled at 7.5. Already after 10 days 92% of the (soluble) COD had been converted into methane. This supports the previous observation that the proteins that were not degraded at high pH can be degraded at lower pH.

5.3.2 Shock increase to pH 9 and 10

Based on the observations above, it was hypothesized that a short shock treatment at elevated pH at the start of a sequencing batch cycle could take advantage of the best of both perspectives: an improved VSS degradation at high pH at the start of a cycle, and a high conversion efficiency of the solubilized COD to VFA at a lower pH later during the cycle. This was tested with pH shock of 9 and 10 during 3.5 hours at an SRT of 5 days. An SRT of 10 days was considered too long because of the risk of introducing methanogenesis.

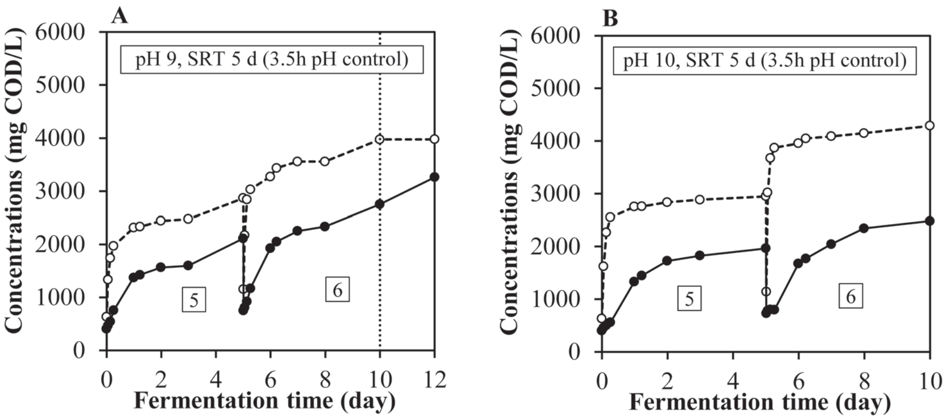

Figure 5.3: (○) Soluble COD concentrations and (●) VFA production during sequencing batch cycles 5–6 fermentation of HL-MBR concentrate, (A) Reactor 1 and (B) Reactor 2 (Numbers in the box indicate the cycle. Dashed line in (A) indicates the end of cycle 6 with an SRT of 5 days.)

Figure 5.3 shows COD solubilization and concomitant VFA production during the cycles 5–6. After a shock of pH 9 had been applied to reactor 1, the pH gradually dropped from 9.0 to 6.8 toward the end of cycles 5–6. The average VFA production was 321 ± 46 mg VFA-COD/g VSS (Table 5.3), which already is a considerable improvement compared to earlier productivities. When a shock to pH 10 was applied to reactor 2 the pH dropped to 8.5 toward the end of cycles 5–6. The average VFA production in this case was somewhat lower (287 ± 30 mg VFA-COD/g VSS), which most likely can be explained by a reduced protein hydrolysis that could not fully recover between pH 10 and 8.5. The difference between these pH shock experiments and sequencing batch cycles operated at a constantly high pH is also reflected in the smaller gap between soluble COD and VFA. At pH 9 and 10 this gaps was 11 ± 3% and 14 ± 5%, respectively (Table 5.3).

In the reactor with a shock of pH 9, VFA production was still increasing at the end of cycles 5–6 (Figure 5.3). It was, therefore, decided to prolong the treatment time in the pH 9 reactor, cycle 6. During an extension of 2 days, the pH gradually dropped from 6.8 to 6.5 and it increased to above 7.0 after 3 days of extension, indicating that methanogenesis could not be avoided any longer. After 2 days of extension, the VFA production increased to 440 mg VFA-COD/g VSS, the highest yield observed in the experiments.

5.3.3 VFA production potential

Using average HL-MBR performance data in terms of COD recovery (75%), this yield of 440 mg VFA-COD/g VSS would translate to a VFA yield of 0.26 g VFA per gram of total sewage COD. Because approximately 50% of the sewage COD that was used is biodegradable, this is equivalent to 0.52 g VFA per gram of biodegradable sewage COD. Obviously, this is a much higher yield than what can be achieved with VFA production from PS and AS generated by CAS systems, because with the HL-MBR and alkaline fermentation combination most of the sewage COD is directed toward VFA and aerobic mineralization of sewage organics is largely avoided.

An even higher VFA yield might be feasible at pH 9 by applying a longer pH shock in combination with a longer SRT, allowing more VSS degradation without the risk of introducing methanogenesis. With the pH shock of 9, a VSS degradation of 54 ± 2% was achieved. However, Table 5.3 shows that for a constant pH of 9 a VSS reduction of at least 68% is feasible. Assuming this additional VSS reduction generates biodegradable soluble COD, this would further increase the yield to 0.33 g VFA per gram of total sewage COD. This also approaches a VFA yield of 35–40%, estimated based on measurements of the biological methane potential of bioflocculated concentrate produced from the same sewage as was used in this study (Akanyeti et al., 2010).

Obviously, the reactors were only operated for a period of 47 days, including a preliminary run and 6 sequencing batch cycles. Probably development and adaptation of the microbial population at pH of 9 or even 10 was limited. Enrichment of alkaliphilic or alkali-tolerant fermenting microorganisms can further enhance the VFA production yield and rate (Ishikawa et al., 2009; Jie et al., 2014a; Zhilina et al., 2004). This therefore presents an interesting topic for future studies.

5.3.4 VFA composition

The VFA composition can be important if the VFA are used as platform chemicals. At pH 9 and 10 the VFA composition was dominated by acetate (58–63% of the total VFA), irrespective of pH control for the full cycle or for a 3.5 hours pH shocked. This was followed by propionate (25–30%) and butyrate (10–15%). These VFA distributions are not very different from those obtained in other studies (Jie et al., 2014b; Liu et al., 2012). At pH 8 propionate was the most prevalent VFA (54 ± 5%), followed by acetate (37 ± 5%) and butyrate (9 ± 0.2%). During fermentation at pH 8, part of acetate was converted into methane. Methanogens can directly use acetate to produce methane, whereas the intermediates propionate and butyrate first need to be converted into acetate.

5.4 Conclusions

A HL-MBR bioflocculation process and alkaline fermentation of the concentrate of this unit were investigated for its potential to produce VFA from sewage organic matter. The highest yield of 440 mg VFA-COD/g VSS was obtained when the sequencing batch fermenter was operated for 7 days and a shock pH of 9 was applied for 3.5 hours. In contrast to a constantly high pH, such a shock enables additional VFA production from proteinaceous COD. Fine-tuning of pH control and possibly longer reactor operation to allow the enrichment of alkaliphilic and alkali-tolerant fermenting microorganisms, may further increase the VFA yield.

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Chapter 6

General discussion and outlook

6.1 Introduction

A growing world population results in a high demand for fresh water and increases the generation of all types of waste, in particular wastewater. Conventional wastewater treatment mainly focuses on producing an effluent quality that meets the discharge guidelines. However, municipal wastewater contains valuable resources including the nutrients nitrogen (N) and phosphorus (P), organic matter, and large amounts of water that can be reused as for example irrigation water. As an alternative to conventional activated sludge (CAS) systems, in this thesis new concepts were investigated that combine wastewater treatment with recovery of these resources.

A preliminary selection from 11 configurations, in which different process units and recently developed technologies were considered, showed that 9 configurations gave low treatment and recovery efficiencies. Therefore, only two novel wastewater treatment configurations were further evaluated in this thesis. In Configuration 1, first bioflocculation was applied to pre-concentrate diluted sewage COD (chemical oxygen demand) for a maximum organic matter recovery. The permeate of the bioflocculation process was subsequently treated by a (cold) partial nitritation/Anammox process to remove N down to levels that meet the discharge guidelines and by a novel cost-effective P recovery technology. Such a P recovery technology could consist of struvite precipitation, which currently is also used to recover P from more concentrated streams such as human urine (Desmidt et al., 2015; Etter et al., 2011). More P recovery technologies are described by Desmidt et al. (2015) and we expect that in the near future a low-cost and high-efficiency P recovery technology from a diluted wastewater will also become available. The bioflocculated sewage organic matter in Configuration 1 was converted to methane in an anaerobic digester, followed by a combined heat and power (CHP) unit to convert the methane to electricity and heat. Configuration 2 used a similar approach with bioflocculation and anaerobic digestion, but N and P in the permeate of the bioflocculation process were assimilated by microalgae. The applicability of both configurations will strongly depend on location, in particular with respect to irradiance and temperature. Both of these conditions have a significant effect on the microalgal biomass productivity, while temperature has a major impact on partial nitritation/Anammox. Thus, both implementations need to be further explored for different locations and wastewater composition.

In this thesis work the two new wastewater treatment configurations were evaluated using two different research methods. The first method was based on numerical simulation to explore their feasibility. This evaluation was done with respect to several key performance indicators (KPIs) and effluent quality as a boundary condition. The novel treatment configurations should: (1) be able to do so throughout the entire year; (2) produce lower CO_2 emission than the CAS system and (3) achieve a higher net energy yield and higher amounts of nutrient recovery compared to the CAS system. Model-based scenario analyses of these wastewater treatment configurations covered the following topics: developing a procedure to design and integrate the individual process units into the most promising configuration using the Netherlands as a case study (Chapter 2), and exploring the two most feasible wastewater treatment configurations for different locations around the globe (Chapter 3).

Complete anaerobic digestion consists of four subsequent steps resulting in the production of methane. During this process volatile fatty acids (VFA) are produced as intermediate compounds. VFA may be preferred over methane as an end product, because VFA are the starting compounds for subsequent production of a wide range of higher value products such as medium-chain fatty acids, bioplastic polyhydroxyalkanoates (PHA) and lipids for biodiesel. Therefore, in this thesis and in addition to numerical simulation, experimental research focused on anaerobic fermentation of bioflocculated sewage organics to VFA (Chapter 4). For this purpose a sequencing batch reactor was used. In addition, alkaline VFA fermentation was investigated to increase the VFA yield (Chapter 5).

6.2 Proposed new wastewater treatment concepts

The potential contribution of Dutch municipal wastewater for energy, N, P, and chemical recovery is illustrated in Table 6.1. Figure 6.1 shows three novel municipal wastewater treatment plant configurations that allow the recovery of these potential resources and at the same time can save considerable amounts of energy.

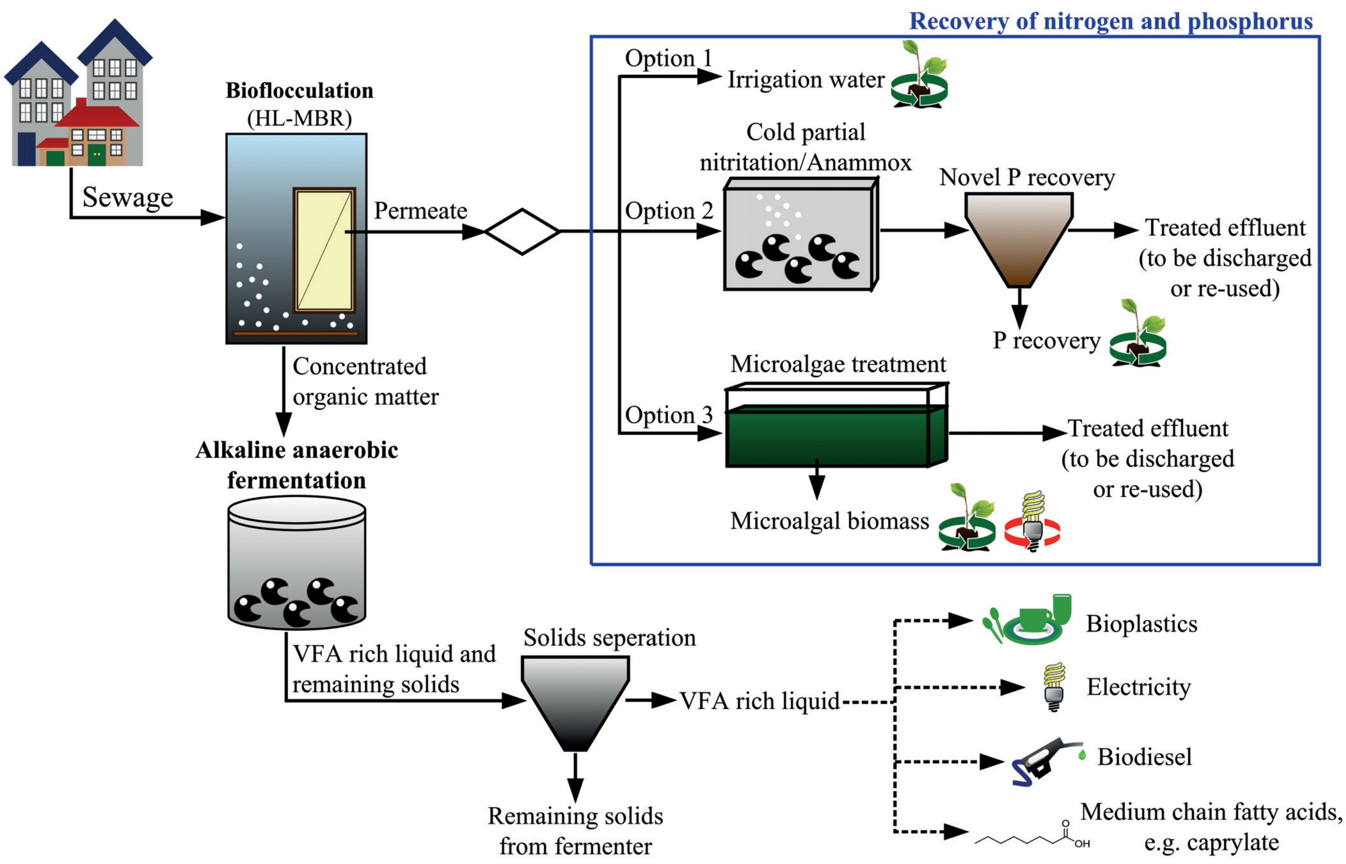

Fig. 6.1: Proposed new municipal wastewater treatment concepts towards energy savings and recovery of resources (VFA, energy and nutrients). Dashed lines indicate examples of possible productions from VFA. ◇ is a decision block of nutrient recovery.

Table 6.1: The annual potential resources in Dutch municipal wastewater, base data for calculations were taken from CBS (2013)

Resource	Annual potential production	Potential products/advantages
1. Water	1,873 million m^3	For irrigation water or industrial process water[a]
2. Phosphorus	13,356 tons of P recovery products in e.g. struvite	Equivalent to about 55% of the Dutch artificial phosphorus fertilizer consumption[b]
3. Nitrogen	877,333 tons of N	Saves 3.25 million GJ of energy otherwise needed for ammonia production with the Haber-Bosch process[c], which is equivalent to the yearly electricity consumption of 300,000 Dutch househoulds[d]
4. Energy[e]	3,372 million kWh, recovered as electricity via methane	Equivalent to electricity use of 1 million Dutch househoulds[d]
5. Chemicals[f]	377,366 tons of VFA	VFA can be used as a platform chemical for products, e.g. medium-fatty acids and bioplastics

[a] Based on DOW (2013).
[b] Based on de Graaff (2010).
[c] Assuming an energy consumption of 37 kJ/g N requires for Haber-Bosch process (Maurer et al., 2003).
[d] Assuming an annual electricity consumption of 3,000 kWh per household (Lilien, 2006).
[e] Assuming chemical energy contained in (biodegradable) organic matter of 1.8 kWh/m^3 of wastewater.
[f] Assuming a ratio of BOD/COD of approximately 0.40 (Henze and Comeau, 2008).

6.3 Up-concentration of sewage organic matter using bioflocculation and membrane filtration

The main technological challenge in recovery of valuable resources from municipal wastewater is the development of cost-effective treatment and recovery technologies that can overcome the problems of low sewage temperatures and diluted valuable compounds (Chapter 1). Therefore, a pre-concentration step is essential for making recovery processes economically feasible. It was hypothesized that bioflocculation in a high-loaded membrane bioreactor (HL-MBR) will concentrate most of the sewage COD, including all settleable solids, suspended COD, colloidal COD and even part of soluble COD, whereas aerobic mineralization of biodegradable COD to

CO_2 can be largely avoided. In this way a maximum organic matter recovery can be obtained. In Chapters 4 and 5 the up-concentration of sewage COD in an HL-MBR was experimentally conducted with an extremely short hydraulic retention time (HRT) of 1 hour and a sludge retention time (SRT) of only 1 day. This MBR system combines two processes: (1) aerobic bioflocculation, in which flocculation is mediated by the presence of microorganisms, to up-concentrate sewage COD, and (2) direct membrane filtration for solids-liquid separation (Akanyeti et al., 2010; Faust et al., 2014a; Faust et al., 2014b). Previous studies towards bioflocculation in HL-MBR's mainly focused on optimization of the flocculation process, i.e. on the effects of operational parameters such as the SRT, HRT and the dissolved oxygen concentration (Faust et al., 2015; Faust et al., 2014a; Sözen et al., 2014).

The bioflocculation in an HL-MBR resulted in very good performance with a COD recovery as high as 75.5% of the sewage COD, a good permeate quality with an average of 49 ± 14 mg COD/L, and only 7.5% of the sewage COD was mineralized (Chapter 4). However, still the underlying mechanisms of the flocculation process are largely unclear and should be further investigated, also because biologically induced flocculation plays an important role in other environmental processes. For instance, the flocculation process has also a strong relation with fouling of the membranes, which remains an important hurdle for a practical implementation (Judd, 2008; Melin et al., 2006). The work of Faust et al. (2014b) studied the membrane resistance in an HL-MBR operated at an SRT between 0.125 and 1 days and an HRT of 0.7 hours with the same sewage as used in the current study. Although the results indicated that fouling in an HL-MBR was largely reversible, in particular at SRTs of 0.5 and 1 days, more research should be dedicated to membrane modules that can remove this fouling continuously at a low energy consumption, in particular because HL-MBR's are operated at high solids concentrations (typically higher than 10 g TSS/L of bioflocculated concentrate).

No mathematical model is available to accurately describe the process of bioflocculation. Information on the mechanisms involved, for example, in the production and degradation of extracellular polymeric substances (EPS) and the distribution of EPS are still limited. Therefore, more experimental work is needed and based on these results a more detailed model of bioflocculation process may be made. In this thesis the assumption was made in Chapters 2 and 3 that there is no temperature effect on the bioflocculation process. However, van den Brink et al.

(2011) showed that temperature should be taken into account when designing a MBR because poor flocculation may occur under extremely low wastewater temperatures, e.g. temperatures below 10°C. Because literature is scarce on this temperature effect, more experimental work is required to elucidate this effect.

6.4 VFA recovery from HL-MBR concentrate

6.4.1 Recovery of VFA produced by alkaline fermentation

It was hypothesized that high pH fermentation combined with a long SRT, allowing for sufficient solubilization of solids and colloidal COD, can improve the VFA yield. The results of Chapter 5 showed that application of a pH shock of 9 in the first 3.5 hours of a sequencing batch cycle followed by a pH uncontrolled phase for 7 days gave a VFA yield of 26% of the sewage COD, the highest yield observed in the experiments. This was much higher than a VFA yield of 15% at an SRT of 5 days without pH control. The main reasons for the higher VFA yield were a reduction of methanogenic activity induced by the high pH levels (Chen et al., 2007; Liu et al., 2012; Yuan et al., 2006) and an improved solids solubilization. At pH 9–10 fermentation sharp increase of soluble COD concentrations in the first 6 hours was observed, which most likely could be explained by a chemical reaction as this cannot be explained by a biological reaction. Feng et al. (2013) hypothesized that at high pH levels hydroxyl anions chemically react with floc structures and cell walls of microorganisms, resulting in proteins dehydration, hydrolysis of carbohydrate and saponification of lipids. Because a more detailed investigation of such chemical reactions was not performed in the scope of this thesis, the underlying mechanisms of alkaline hydrolysis of the HL-MBR concentrate remain unclear and should be further explored.

The results of Chapter 5 also showed that at constant pH of 9–10 a considerable amount of (soluble) proteins were not converted into VFA. Two hypothesizes were made: (1) proteins can lose their primary-quaternary structure at elevated pH levels and are no longer amenable to enzymatic hydrolysis (Rami and Udgaonkar, 2001) and (2) at pH 9–10 is suppressed production of proteases or activity of these proteases. Liu et al. (2012) showed that alkaline pH levels of 9–12 were beneficial for the solubilization and biodegradation of proteins, but Maspolim et al. (2015) reported a reduction in hydrolytic enzymatic activity of protease at pH 9–11. The reason for these different observations remains unclear and asks for future studies. To continue work in line with this thesis, a more detailed chemical characterization of the remaining effluent produced from high pH fermenter of the HL-MBR concentrate is required. If indeed proteins are the main compounds in the remaining fermenter effluent, future research needs to be focused on how to improve on the degradability of these proteins at high pH levels. For instance, the proteolytic activity at high pH could be measured, which will help to understand the mechanism for VFA production at high pH and may provide information to further increase the VFA yield.

6.4.2 Maximize VFA yield and production

In Chapter 5 it was found that a VFA yield of 33% of the sewage COD can be expected from high pH anaerobic fermentation of the HL-MBR concentrate. Two different operational systems can be considered. The first system uses a high pH shock at the start of a sequencing batch cycle, followed by a pH uncontrolled phase. This has two important advantages: (1) solids degradation is improved during the first phase compared to without pH control and (2) proteins that were not degraded at pH 9–10 can be subsequently converted into VFA at the lower pH in the second phase. More application research is required to (1) fine-tune these pH levels, (2) determine the time period of the pH shock and (3) find out the optimal SRT allowing for a maximum VFA yield. Knowing the optimal conditions will allow a maximum solids degradation and high proteolytic activity without the risk of introducing methanogenic activity. The second system would be operated at constantly high pH throughout the batch cycle with fermentative microorganisms adapted to such a high pH, as are commonly found in nature. It is hypothesized that such inocula from alkaline natural environments also contain a high proteolytic activity at high pH levels. At the moment, a conclusion about the most promising mixed cultures cannot be made. Table 6.2 at least shows that there are different species of VFA-producing alkaliphilic microorganisms in various environments. Because information about degradation of proteins at high pH levels in those species remains unclear and thus this should be first experimentally investigated. Although a constant high pH fermentation can be advantageous over a high pH shock with respect to high solids degradation and inhibition of methanogens, the implementation of a high pH shock fermentation seems to be a more promising method in terms of consumption of chemicals (caustic), or in terms of energy consumption in case electrochemical methods are applied for extraction of the anionic VFA's at high pH.

Table 6.2: Examples of possible alkaliphilic anaerobic fermenting cultures for future studies under different range and optimum conditions of pH, temperature (T) and concentration of Na^+

Microorganisms	Fermentation products	Isolation origin	pH range (optimum)	T range (optimum) (°C)	Na^+ concentration (optimum) (M Na^+)	Reference
Proteinivorax tanatarense	acetate, formate, propionate, succinate, n- and iso-butyrate, iso-valerate, H_2, 2-methylbutyrate, NH_4	Alkaline Lake Tanatar VI, Russia	7.6–10.5 (8.8)	6–52 (32–38)	0.4–3.6 (2–3)	Kevbrin et al. (2013)
Alkalibacterium thalassium	Lactate, formate, acetate, ethanol	Seashore of Samet Island, Thailand	7.0–11.0 (9.0)	10–42.5 (37)	0–0.75 [a] (0.07–0.17)	Ishikawa et al. (2009)
Alkalibacterium pelagium	Lactate, formate, acetate, ethanol	Seashore of Chang Island, Thailand	7.0–11.0 (9.0–9.5)	10–47.5 (37)	0–1.16 [a] (0.03–0.10)	Ishikawa et al. (2009)
Alkalibacterium putridalgicola	Lactate, formate, acetate, ethanol	Seashore of Samet Island, Thailand	6.5–10.0 (8.0–9.0)	-1.8 and 40–45 (37–40)	0 to 1.23–1.37 [a] (0.14–0.27)	Ishikawa et al. (2009)
Alkalibacterium kapii	Lactate, formate, acetate, ethanol	Ka-pi (salted & fermented shrimp paste), Thailand	6.0–6.5 to 10 (8.5–9.0)	5–10 and 40–42.5 (25–37)	0 to 1.30–1.43 [a] (0.10–0.17)	Ishikawa et al. (2009)
Alkalibacterium indicireducens	Lactate, formate, acetate	Tokushima Prefecture, Japan	9.0–12.3 (9.5–11.5)	15–35 (20–30)	0–0.96 [a] (0.07–0.75)	Yumoto et al. (2008)
Alkaliflexus imshenetskii	propionate, acetate, succinate	Soda Lake	7.2–10.2 (8.5)	10–44 (35)	0.27–0.44 (0.35)	Zhilina et al. (2004)
Anoxynatronum sibiricum	Acetate and ethanol	Lake Nizhnee Beloe, Transbaikal region, Russia	7.1–10.1 (9.1)	25–41 (35)	0.08–1.30 (0.25–0.86)	Garnova et al. (2003)
Marinilactibacillus psychrotolerans	Lactate, formate, acetate, ethanol	Temperate and subtropical areas, Japan	6.0–10.0 (8.0–9.5)	-1.8 to 40–45 (37–40)	0 to 1.16–1.40 [a] (0.14–0.26)	Ishikawa et al. (2003)
Amphibacillus fermentum	Formate, acetate, ethanol	Lake Magadi, Kenya	7.0–10.5 (8.0–9.5)	18–56 (36–38)	0.17–3.3 (1.87)	Zhilina et al. (2001)
Amphibacillus tropicus	Formate, acetate, ethanol	Lake Magadi, Kenya	8.5–11.5 (9.5–9.7)	18-56 (38)	0.17–3.6 (1–1.87)	Zhilina et al. (2001)
Tindallia magadii	Acetate, formate, propionate, iso-valerate, H_2 , NH_4	Lake Magadi, Kenya	7.5–10.5 (8.5)	19–47 (37)	(0.5–1.0)	Kevbrin et al. (1998)

[a] Na^+ concentration was calculated based on a percentage of NaCl, where 1% (w/v) of NaCl was equal to 10 g NaCl/L (0.17 M NaCl, 0.07 M Na^+).

In our experiments the bioflocculated sewage organic matter had a concentration of 10 g COD/L, from which about 3.5 g VFA-COD/L could be produced (Chapter 5). However, a more concentrated substrate should be considered to make recovery processes economically feasible, possibly with a COD concentration of 12–20 g/L or higher (Gurieff and Lant, 2007). In an HL-MBR, this can be accomplished by reducing the HRT. The VFA production from a 20 g COD/L of bioflocculated concentrate becomes a promising candidate as this will increase VFA production up to 7 g VFA-COD/L. This indicates that in an HL-MBR the HRT needs to be decreased from 1 to 0.5 hours, which can be reasonably performed (Faust et al., 2014b). However, the feasibility of an HL-MBR with such a low HRT needs to be further investigated with respect to membrane fouling, oxygen limitation and the extent of membrane area. In addition, at HRT's below 0.5 hours new membrane modules need to be developed because current modules would be too big to fit into the bioflocculation reactor (Faust, 2014). It should also be noted that a more concentrated substrate would lead to a higher free ammonia in an anaerobic fermenter, in particular at high pH may cause toxicity to the fermenting microorganisms (Sousa et al., 2015), and this should be further investigated.

Apart from optimizing the VFA yield, to achieve higher VFA productivities, water boards may consider the use of other feed substrates, such as food waste addition as a co-substrate for high pH anaerobic fermentation. However, the effect of the composition of co-substrate addition on recovery efficiency and VFA composition needs to be further investigated to be able to predict which co-substrates are suitable candidates for this.

6.4.3 Alkaline homoacetogenesis

Stimulation of homoacetogenesis, which is the formation of acetate from inorganic carbon and H_2, could be another advantage of high pH fermentation because it would enhance the VFA yield. Modestra et al. (2015) studied VFA production from an enriched homoacetogenic culture at different pH levels of 5, 6.5, 8.5 and 10. They found that at pH 10 the production of VFA was approximately two times of that at pH 5. This was explained by a higher inorganic carbon availability. However, in the present study the contribution of homoacetogenesis at high pH compared to low pH was not determined and thus presents an interesting topic for future studies.

6.4.4 VFA extraction

The VFA that is produced causes product inhibition and thus negatively affects VFA productivity (Siegert and Banks, 2005; Wang et al., 2009). Therefore, continuous extraction of VFA from the fermenter is needed to obtain adequate VFA yields. This implies that continuous solids separation should be combined with continuous VFA extraction from the remaining bulk liquid. Several techniques can be used for this VFA extraction such as adsorption, solvent extraction, chemical precipitation, and electrodialysis (ED) (Huang et al., 2007; López-Garzón and Straathof, 2014). Of these techniques, ED extraction is a promising technology as the VFA produced at high pH are in ionized form. Bipolar-membrane electrodialysis (BMED) and electro-electrodialysis (EED) are a kind of ED technique, which have been extensively studied for the recovery of organic acids, because these two technologies do not require addition of chemicals (Bailly, 2002; Vertova et al., 2009; Wang et al., 2010). BMED and EED also give an opportunity to simultaneously produce a caustic solution, which can be used to keep high pH levels in the anaerobic fermenter. However, further investigation on these two methods is still needed, in particular the selectivity for individual VFA, operational costs and energy consumption. It should also be noted that lower pH levels in a "pH shock" configuration may lead to a higher unionized VFA than in a "constant high pH" configuration. In our experiments, with a "pH shock" configuration the pH dropped to about 7. Based on the pKa values of acetate, propionate and butyrate, ED extraction can still be applied because more than 90% of the generated VFA will exist in ionized form (López-Garzón and Straathof, 2014).

To continue work in line with this thesis, three possible alternatives for VFA application should be considered for future studies. According to the first alternative, the VFA rich liquid can be used to directly produce higher value products, for example medium-chain fatty acids (Grootscholten et al., 2014) and PHA (Morgan-Sagastume et al., 2014). In the second alternative, a pre-concentration of the VFA rich liquid can be used to increase the amount of end products or make VFA recovery processes economically feasible (Wang et al., 2010). In both alternatives the VFA composition becomes important with respect to yield and quality of the end products, such as PHA (Albuquerque et al., 2011; Dias et al., 2006) and electricity generated in a microbial fuel cell (Lee et al., 2014). For example, a mixture of acetate and propionate (50:50%) led to the production of PHA copolymers with a storage yield of 0.37 g PHA/g substrate, while a homopolymer of polyhydroxybutyrate (PHB) was obtained from only acetate as a substrate but the storage yields varied from 0.22–0.56 g/g substrate (Dias et al., 2006; Lemos et al., 2006). The last alternative would be to separate a mixture of VFA to single acids, as this would enhance the value of recovery product. A life cycle assessment and financial analysis of a mixed VFA production and a single acid production needs to be performed.

6.4.5 Fermenter effluent

For a treatment plant of 100,000 population equivalents, treating 13,000 m^3 of wastewater per day, a HL-MBR would produce 520 m^3/day of concentrate that in line with this study will be treated in a high pH anaerobic fermenter. At a VFA yield of 33% of the sewage COD (Chapter 5), after extraction of the valuable VFA, 5.5% of the sewage COD would remain in the fermenter effluent as non-biodegradable soluble COD (from Figure 4.5 in Chapter 4 and Table 5.3 in Chapter 5) and 37% as particulate COD. The solids concentration of 4.3 g TSS/L (Chapter 5) in the fermenter effluent is much lower than obtained from an anaerobic digestion treating a mixture of PS and AS, i.e. approximately 15–40 g TSS/L of the digester effluent (Metcalf and Eddy, 2004). The settleability and dewaterability of the solids were not investigated in the present study and therefore more experimental data for these parameters are required before a selection of a proper separation technique can be made.

For a treatment plant of 100,000 population equivalents, treating 13,000 m^3 of wastewater per day, the load of waste solids produced by the fermenter is 2.2 tons TSS/day (4.3 kg TSS/m^3 * 520 m^3/day), which is at least three times smaller than for CAS systems. It is hypothesized that a lower solids production may be caused by the high degree of solids degradation at high pH levels in the fermenter. The dewatered cake may be reused as organic fertilizer. However, further research is required towards the distribution of heavy metals, pathogens and micropollutants in the HL-MBR and high pH fermentation processes as well as in the end products, and this should be compared with waste streams from CAS systems. Although this should be further quantified, it is hypothesized that the high pH in the fermenter can help to reduce the levels of pathogens in the fermenter effluent (Magri et al., 2015; Petruzzelli et al., 2015).

The concentration of non-biodegradable COD of the water remaining after solids dewatering can be as high as 690 mg COD/L. Recirculation of this water to the HL-MBR is not an option because it will only accumulate in the treatment system and result in more fouling. The load of this COD is very small compared to the COD load in the permeate of the HL-MBR. We therefore expect that mixing this waste stream with the HL-MBR permeate is possible without causing problems for subsequent treatment by partial nitritation/Anammox or by microalgae.

6.5 Nutrient recovery from HL-MBR permeate

HL-MBR permeate is obviously free from solids, including pathogens. In Chapter 4 it was found that it still contains 90% of the sewage NH_4-N and PO_4-P. Figure 6.1 shows three options to remove or recover these nutrients.

6.5.1 Irrigation water

In the first option, because of high concentrations of NH_4-N and PO_4-P in the HL-MBR permeate and because it is free of pathogens, the HL-MBR permeate can be used as irrigation water. In this way the nitrogen and phosphorus cycles can be closed between households and agriculture. However, micropollutants such as pharmaceuticals and personal care products are only partially or not at all removed and may limit reuse as irrigation water. In fact, because of the shorter SRT of the HL-MBR compared to CAS systems the removal efficiency of these compounds may be lower and advanced post-treatment will be required.

6.5.2 (Cold) partial nitritation/Anammox followed by P-recovery

A bio-based treatment and recovery approach is suggested as the second option in Figure 6.1 that can save considerable amounts of energy and recover phosphorus. In particular P recovery is very important because it is expected to become a scarce resource in the near future (Cordell et al., 2011). The recovery of N is less urgent than that of P, and therefore novel N recovery technologies may not be sustainable and cost-effective at low sewage N concentrations. Therefore, the main technological challenge in sewage N removal is the development of less energy consumption technology than in CAS systems. Partial nitritation/Anammox technology can save at least 50% aeration energy compared to a conventional nitrification/denitrification process (Fux and Siegrist, 2004). Based on the study by Hendrickx et al. (2014), who showed that the Anammox process is feasible at a temperature of 10°C, in this thesis it was assumed that cold partial nitritation/Anammox can be applied if the temperature of wastewater is above 10°C. However, this concept still needs further optimization. In particular the partial nitritation process at temperatures down to 10°C is challenging and oxygen control becomes crucial to avoid nitrate production (Hao et al., 2002). This implies that partial nitritation/Anammox cannot be applied in the winter period, for example, in Northern America, Eastern Europe and Northeastern Asia.

In the current study novel P recovery technologies from the HL-MBR permeate were not further substantiated. The main challenge for this is development of a cost-effective technology that can work at low sewage temperatures and low phosphorus concentrations.

6.5.3 Microalgae treatment

The potential to produce concentrated organic N and P using microalgae cultivation as a third option is determined by the production location (Chapters 2 and 3). In the Netherlands, a microalgae system for municipal wastewater treatment is not applicable because of a limited light availability, and the low temperatures and irradiance in the winter period. Nevertheless, in tropical regions, for example Southeastern Asia, Southern America, Western and Eastern Africa, microalgae treatment seems to be applicable. With Thai temperature and photon flux density (PFD) conditions as an example, a microalgae reactor requires the area of 2.2 m^2/person in the winter period, the lowest area requirement observed in the current study. However, this area requirement is still much higher than for a conventional municipal wastewater treatment plant (WWTP), i.e. 0.2–0.4 m^2/person (Boelee et al., 2012). This implies that a microalgae treatment may be feasible in rural areas, but this would not be economical feasible because of a limited volume of wastewater production. On larger scales WWTP, i.e. located in or nearby cities, land availability and costs are limiting factors. In this case a microalgae treatment would be economical feasible, if the applications of microalgal biomass will be able to produce a very high value product, such as carotenoids, biocement, aquaculture feed, dietary supplement, or cosmetics (Dessy et al., 2011; Enzing et al., 2014). However, contamination of the end products by municipal wastewater compounds should be eliminated, which will increase the complexity and costs of the process, because in this case only the nutrients should be allowed to come into contact with the microalgae.

Area requirement is also directly related to seasonal conditions. Differences in temperature and PFD between summer and winter periods become important when designing a microalgae treatment because of economic feasibility, in particular area requirement in the winter period. In this thesis a quantitative glocal assessment of a microalgae treatment showed that with Indian temperature and PFD conditions as an example, the area requirement in the winter period was almost 5 times higher than in the summer period. This implies that two different wastewater treatment plant configurations need to be implemented, for example a microalgae treatment can be used for the summer period, while CAS systems or a combination of bioflocculation and (cold) partial nitritation/Anammox is needed for the winter period. In practice municipal WWTP with two different configurations may not be realistic due to the high investment costs and complexity, and thus CAS systems are more preferable with respect to year round feasibility.

Although light is an essential growth factor for microalgae, photo-inhibition commonly occurs under extreme light intensities, typically above a PFD of 650 μmol photons/m^2/s (Beardall and Raven, 2013). In addition, a high light intensity may heat up the water in microalgae reactors to levels which are too high to allow microalgae growth. In this case the reactor even needs to be cooled. For example, a maximum photosynthetic productivity of green microalga *Chlorella sorokiniana* can be achieved at a temperature of 38.1°C, whereas it will not survive at temperatures above 49.7°C (Morita et al., 2000).

Another practical challenge to implement microalgae system for municipal wastewater treatment is nutrient composition. When typical municipal wastewater characteristics were used in a quantitative scenario-based analysis, the N target effluent of 2.2 mg N/L was taken because the sewage N and not the sewage P concentration determines the biomass productivity per liter of wastewater. However, wastewater characteristics may vary from location to location caused by differences in precipitation, water scarcity and separation of storm water. Clearly, the nutrient composition of the sewage may dictate the optimum treatment configuration, including the feasibility of microalgae systems.

6.6 Conclusions

This thesis focused on exploring new municipal wastewater treatment concepts that help to improve energy saving and allow recovery of valuable resources. Modelling results show that configurations with bioflocculation and (cold) partial nitritation/Anammox can be operated if the wastewater temperature is above 10°C and microalgae treatment can be applied year round only in tropical regions that are close to the equator line. The results obtained by experiment work show that a combined process of bioflocculation HL-MBR and subsequent alkaline anaerobic fermentation for VFA production is technologically feasible. However, future research should be conducted, in particular on the cost analysis, market opportunity for VFA, extraction technology, and quality of the end products.

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Appendix A

Calculations of mass fluxes of COD, N and P in Configuration 1 with bioflocculation, partial nitritation/Anammox, anaerobic digestion and CHP unit (Figure 2.3)

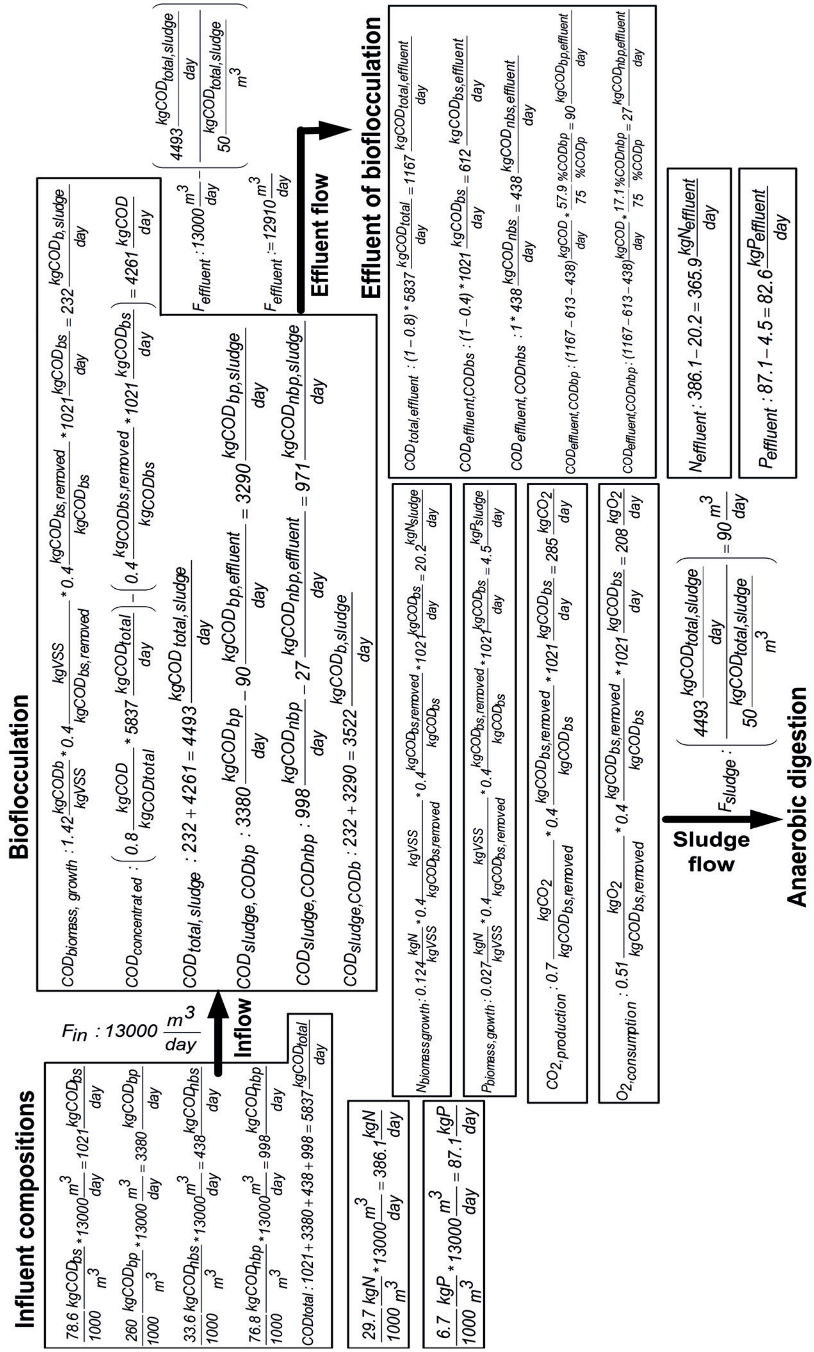

Figure A.1: Calculation of mass fluxes of COD, N, and P in bioflocculation

Figure A.2: Calculation of mass fluxes of COD, N, and P in cold partial nitritation and Anammox

Cold partial nitritation and Anammox

Inflow

$$12910 \frac{m^3}{day}$$

$$N_{total,removal} : 365.9 \frac{kgN_{effluent,BF}}{day} * 0.9 \frac{kgN_{removed}}{kgN_{effluent,BF}} = 329 \frac{kgN_{removed}}{day}$$

$$N_{2,production} : 329 \frac{kgN_{removed}}{day} * 0.885 \frac{kgN_2}{kgN_{removed}} = 291.5 \frac{kgN_2}{day}$$

$$NO_{3,production} : 329 \frac{kgN_{removed}}{day} * 0.11 \frac{kgNO_3}{kgN_{removed}} = 36 \frac{kgNO_3}{day}$$

$$COD_{sludge,N-removal} : 1.42 \frac{kgCOD}{kgVSS} * 0.05 \frac{kgVSS}{kgN_{removed}} * 329 \frac{kgN_{removed}}{day} = 23 \frac{kgCOD_{sludge,N-removal}}{day}$$

$$COD_{removed,PN} : 0.35 \frac{kgCOD_{removed,PN}}{kgCOD_{total,effluent}} * \left(1167 \frac{kgCOD_{total,effluent,BF}}{day} - 23 \frac{kgCOD_{sludge}}{day}\right) = 400 \frac{kgCOD_{removed,PN}}{day}$$

$$COD_{removed,AN} : 0.05 \frac{kgCOD_{removed,AN}}{kgCOD_{total,effluent}} * \left(1167 \frac{kgCOD_{total,effluent}}{day} - 23 \frac{kgCOD_{sludge}}{day} - 400 \frac{kgCOD_{sludge}}{day}\right) = 37 \frac{kgCOD_{removed,AN}}{day}$$

$$COD_{sludge,COD-removal} : 1.42 \frac{kgCOD}{kgVSS} * 0.4 \frac{kgVSS}{kgCOD_{removed}} * \left(400 \frac{kgCOD_{removed,PN}}{day} + 37 \frac{kgCOD_{removed,AN}}{day}\right) = 249 \frac{kgCOD_{sludge,COD-removal}}{day}$$

$$COD_{total,sludge} : 249 \frac{kgCOD_{sludge,COD-removal}}{day} + 23 \frac{kgCOD_{sludge,N-removal}}{day} = 272 \frac{kgCOD_{total,sludge}}{day}$$

$$N_{biomass,growth(N-removal)} : 0.09 \frac{kgN}{kgVSS} * 0.05 \frac{kgVSS}{kgN_{removed}} * 329 \frac{kgN_{removed}}{day} = 1.5 \frac{kgN_{sludge,N-removal}}{day}$$

$$N_{biomass,growth(COD-removal)} : 0.124 \frac{kgN}{kgVSS} * 0.4 \frac{kgVSS}{kgCOD_{removed}} * \left(400 \frac{kgCOD_{removed,PN}}{day} + 37 \frac{kgCOD_{removed,AN}}{day}\right) = 21.7 \frac{kgN_{sludge,COD-removal}}{day}$$

$$N_{total,biomass,growth} : 1.5 \frac{kgN_{sludge,N-removal}}{day} + 21.7 \frac{kgN_{sludge,COD-removal}}{day} = 23.2 \frac{kgN_{sludge}}{day}$$

$$P_{biomass,growth(N-removal)} : 0.02 \frac{kgP}{kgVSS} * 0.05 \frac{kgVSS}{kgN_{removed}} * 329 \frac{kgN_{removed}}{day} = 0.33 \frac{kgP_{sludge,N-removal}}{day}$$

$$P_{biomass,growth(COD-removal)} : 0.027 \frac{kgP}{kgVSS} * 0.4 \frac{kgVSS}{kgCOD_{removed}} * \left(400 \frac{kgCOD_{removed,PN}}{day} + 37 \frac{kgCOD_{removed,AN}}{day}\right) = 4.72 \frac{kgP_{sludge,COD-removal}}{day}$$

$$P_{total,biomass,growth} : 0.33 \frac{kgP_{sludge,N-removal}}{day} + 4.72 \frac{kgP_{sludge,COD-removal}}{day} = 5.1 \frac{kgP_{sludgel}}{day}$$

Figure A.2: Calculation of mass fluxes of COD, N, and P in cold partial nitritation and Anammox (continued)

Cold partial nitritation and Anammox (continued)

$$O_{2,consumption,N-removal}: 329\frac{kgN_{removed}}{day} * 1.95\frac{kgO_2}{kgN_{removed}} = 641\frac{kgO_2}{day}$$

$$O_{2,consumption,COD-removal}: 0.51\frac{kgCO_2}{kgCOD_{removed}} * \left(400\frac{kgCOD_{removed,PN}}{day} + 37\frac{kgCOD_{removed,AN}}{day}\right) = 223\frac{kgO_2}{day}$$

$$O_{2,total,consumption}: 641\frac{kgO_2}{day} + 223\frac{kgO_2}{day} = 864\frac{kgO_2}{day}$$

$$CO_{2,need,N-removal}: 329\frac{kgN_{removed}}{day} * 0.09\frac{kgCO_2}{kgN_{removed}} = 29\frac{kgCO_{2,need}}{day}$$

$$CO_{2,production,COD-removal}: 0.7\frac{kgCO_2}{kgCOD_{removed}} * \left(400\frac{kgCOD_{removed,PN}}{day} + 37\frac{kgCOD_{removed,AN}}{day}\right) = 306\frac{kgCO_{2,production}}{day}$$

$$CO_{2,total,production}: 306\frac{kgCO_{2,production}}{day} - 29\frac{kgCO_{2,need}}{day} = 277\frac{kgCO_{2,production}}{day}$$

Effluent of cold partial nitritation and Anammox

Effluent flow

$$12910\frac{m^3}{day}$$

$$COD_{total,effluent}: 1167\frac{kgCOD_{total,effleunt,BF}}{day} - \left(23\frac{kgCOD_{sludge,N-removal}}{day} + 437\frac{kgCOD_{removed,AN+PN}}{day}\right) = 707\frac{kgCOD_{total,effluent}}{day}$$

$$N_{total,effluent}: 365.9\frac{kgN_{total,effleunt,BF}}{day} - 329\frac{kgN_{removed}}{day} - 21.7\frac{kgN_{sludge,COD-removal}}{day} + 36\frac{kgNO_3}{day} = 51.2\frac{kgP_{total,effluent}}{day}$$

$$P_{total,effluent}: 82.6\frac{kgP_{total,effleunt,BF}}{day} - \left(0.33\frac{kgP_{sludge,N-removal}}{day} + 4.72\frac{kgP_{sludge,COD-removal}}{day}\right) = 77.5\frac{kgP_{total,effluent}}{day}$$

Figure A.3: Calculation of mass fluxes of COD, N, and P in anaerobic digestion and CHP unit

$$F_{in}: 90 \frac{m^3}{day}$$

Anaerobic digestion and Combined heat and power (CHP)

$$COD_{removed} : 0.7 \frac{kgCODb}{kgCOD_{sludge,CODb}} * 3522 \frac{kgCOD_{sludge,CODb}}{day} = 2465 \frac{kgCOD_{b,removed}}{day}$$

$$CO_{2,production} : 0.64 \frac{kgCO_2}{kgCOD_{b,removed}} * 2465 \frac{kgCOD_{b,removed}}{day} = 1578 \frac{kgCO_2}{day}$$

$$COD_{biomass,growth} : 1.42 \frac{kgCOD}{kgVSS} * 0.058 \frac{kgVSS}{kgCOD_{removed}} * 2465 \frac{kgCOD_{b,removed}}{day} = 201 \frac{kgCOD_{biomass,growth}}{day}$$

$$COD_{total,sludge} : 201 \frac{kgCOD_{biomass,\ growth}}{day} + 971 \frac{kgCOD_{nbp,\ sludge,\ BF}}{day} = 1172 \frac{kgCOD_{total,sludge}}{day}$$

$$N_{biomass,growth} : 0.124 \frac{kgN}{kgVSS} * 0.058 \frac{kgVSS}{kgCOD_{removed}} * 2465 \frac{kgCOD_{b,removed}}{day} = 17.5 \frac{kgN_{biomass,growth}}{day}$$

$$P_{biomass,growth} : 0.027 \frac{kgP}{kgVSS} * 0.058 \frac{kgVSS}{kgCOD_{removed}} * 2465 \frac{kgCOD_{b,removed}}{day} = 3.9 \frac{kgP_{biomass,growth}}{day}$$

$$CH_{4,production} : 0.23 \frac{kgCH_4}{kgCOD_{b,removed}} * 2465 \frac{kgCOD_{b,removed}}{day} = 566 \frac{kgCH_4}{day}$$

Combined heat and power (CHP)

$$Electricity_{recovery} : 0.38 \frac{kgCH_4}{kgCH_{4,production}} * 566 \frac{kgCH_{4,production}}{day} * 13.9 \frac{kWh}{kgCH_4} = 2989 \frac{kWh}{day}$$

$$Heat_{recovery} : 0.40 \frac{kgCH_4}{kgCH_{4,production}} * 566 \frac{kgCH_{4,production}}{day} * 13.9 \frac{kWh}{kgCH_4} = 3147 \frac{kWh}{day}$$

$$Energy_{loss} : \left(1 - 0.38 - 0.40 \frac{kgCH_4}{kgCH_{4,production}}\right) * 566 \frac{kgCH_{4,production}}{day} * 13.9 \frac{kWh}{kgCH_4} = 1731 \frac{kWh}{day}$$

$$CO_{2,production} : 2.75 \frac{kgCO_{2,production}}{kgCH_4} * 566 \frac{kgCH_{4,production}}{day} = 1556 \frac{kgCO_{2,production}}{day}$$

Reject water of anaerobic digestion

$$F_{reject-water} : 90 \frac{m^3}{day}$$

$$COD_{reject-water} : 4493 \frac{kgCOD_{total,sludge,\ BF}}{day} - 2465 \frac{kgCOD_{b,removed}}{day} - 971 \frac{kgCOD_{nbp,\ sludge,\ BF}}{day} = 1057 \frac{kgCOD_{reject-water}}{day}$$

$$N_{reject-water} : 20.2 \frac{kgN_{sludge,BF}}{day} - 17.5 \frac{kgN_{biomass,growth}}{day} = 2.7 \frac{kgN_{reject-water}}{day}$$

$$P_{reject-water} : 4.5 \frac{kgP_{sludge,\ BF}}{day} - 3.9 \frac{kgP_{biomass,\ growth}}{day} = 0.6 \frac{kgP_{reject-water}}{day}$$

Figure A.4: Calculation of mass fluxes of COD, N, and P in P-recovery and effluent of treated water

P recovery and effluent of treated water

Inflow $12910\,\frac{m^3}{day}$

P recovery

$$P_{recovery} : 0.90\,\frac{kgP}{kgP_{total,effluent}} * 77.5\,\frac{kgP_{total,effluent,AN}}{day} = 69.7\,\frac{kgP_{reocvery}}{day}$$

$$P_{total,effluent} : 77.5\,\frac{kgP_{total,effluent,AN}}{day} - 69.7\,\frac{kgP_{reocvery}}{day} = 7.8\,\frac{kgP_{total,effluent}}{day}$$

Effluent flow $12910\,\frac{m^3}{day}$

Effluent of Treated water

$$COD_{effluent} : 707\,\frac{kgCOD_{total,effluent,AN}}{day} \div 12910\,\frac{m^3}{day} * 1000\,\frac{g}{kg} = 54.6\,\frac{gCOD}{m^3}\left(\frac{mgCOD}{L}\right)$$

$$N_{effluent} : 51.2\,\frac{kgN_{total,effluent,AN}}{day} \div 12910\,\frac{m^3}{day} * 1000\,\frac{g}{kg} = 4.0\,\frac{gN}{m^3}\left(\frac{mgN}{L}\right)$$

$$P_{effluent} : 7.8\,\frac{kgP_{total,effluent}}{day} \div 12910\,\frac{m^3}{day} * 1000\,\frac{g}{kg} = 0.6\,\frac{gP}{m^3}\left(\frac{mgP}{L}\right)$$

Appendix B

Analytical evaluation of normalized sensitivity coefficients

Analytical evaluations of the normalized sensitivity coefficients of area requirement (A) with respect to biomass yield on light energy ($Y_{X,E}$) and biomass maintenance coefficient ($m_{E,X}$) were obtained from the partial derivatives of A with respect to $Y_{X,E}$ and $m_{E,X}$, respectively.

That is,

$$S_{A,Y_{X,E}} = \left(\frac{\partial A}{\partial Y_{X,E}}\right)\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right)$$

$$= \left(\frac{\partial A}{\partial \mu_T}\;\frac{\partial \mu_T}{\partial Y_{X,E}}\right)\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right)$$

$$= \left(\frac{\partial}{\partial \mu_T}\left(\frac{F_W}{L*\mu_T}\right)\;\frac{\partial}{\partial Y_{X,E}}\left[\left(r_{E,X}-m_{E,X}\right)*f_T*Y_{X,E}\right]\right)\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right)$$

$$= \left(-\frac{F_W}{L*\mu_T{}^2}\right)\left(\left(r_{E,X}-m_{E,X}\right)*f_T\right)\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right) \qquad \textbf{(B.1)}.$$

Substitute μ_T from Eq. 3.3 into Eq. B.1, so that

$$S_{A,Y_{X,E}} = \left(\left(\frac{-F_W}{L}\right)\frac{1}{\left[\left(r_{E,X}-m_{E,X}\right)*Y_{X,E}*f_T\right]^2}\right)\left(\left(r_{E,X}-m_{E,X}\right)*f_T\right)\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right)$$

$$= \left(\frac{-F_W}{L}\right)\frac{1}{\left(r_{E,X}-m_{E,X}\right)*f_T*\left(Y_{X,E}\right)^2}\left(\frac{\bar{Y}_{X,E}}{\bar{A}}\right) \qquad \textbf{(B.2)}.$$

Substitute $r_{E,X}$ from Eq. 3.2 and subsequently $C_{X,N}$ from Eq. 3.1 into Eq. B.2, leading to

$$S_{A,Y_{X,E}} = \frac{-F_W*\bar{Y}_{X,E}}{L*\left(\frac{PFD_{in}*F_N}{L*\left(N_{in}-N_{eff}\right)}-m_{E,X}\right)*f_T*\left(Y_{X,E}\right)^2*\bar{A}} \qquad \textbf{(B.3)}.$$

Similarly,

$$S_{A,m_{E,X}} = \left(\frac{\partial A}{\partial m_{E,X}}\right)\left(\frac{\overline{m}_{E,X}}{\overline{A}}\right)$$

$$= \left(\frac{\partial A}{\partial \mu_T}\ \frac{\partial \mu_T}{\partial m_{E,X}}\right)\left(\frac{\overline{m}_{E,X}}{\overline{A}}\right)$$

$$= \left(\frac{\partial}{\partial \mu}\left(\frac{F_W}{L * \mu_T}\right)\ \frac{\partial}{\partial m_{E,X}}\left[\left(r_{E,X} - m_{E,X}\right) * f_T * Y_{X,E}\right]\right)\left(\frac{\overline{m}_{E,X}}{\overline{A}}\right)$$

$$= \left(-\frac{F_W}{L * \mu_T^{\,2}}\right)\left(-f_T Y_{X,E}\right)\left(\frac{\overline{m}_{E,X}}{\overline{A}}\right) \qquad \textbf{(B.4)}.$$

Substitute μ_T from Eq. 3.3 into Eq. B.4, so that

$$S_{A,m_{E,X}} = \frac{F_W * f_T Y_{X,E} * \overline{m}_{E,X}}{L * \left[\left(r_{E,X} - m_{E,X}\right) * f_T * Y_{X,E}\right]^2 * \overline{A}}$$

$$= \frac{F_W * \overline{m}_{E,X}}{L * \left(r_{E,X} - m_{E,X}\right)^2 * f_T * Y_{X,E} * \overline{A}} \qquad \textbf{(B.5)}.$$

Substitute $r_{E,X}$ from Eq. 3.2 and subsequently $C_{X,N}$ from Eq. 3.1 into Eq. B.5, leading to

$$S_{A,m_{E,X}} = \frac{F_W * \overline{m}_{E,X}}{L * \left(\frac{PFD_{in} * F_N}{L * \left(N_{in} - N_{eff}\right)} - m_{E,X}\right)^2 * f_T * Y_{X,E} * \overline{A}} \qquad \textbf{(B.6)}.$$

The absolute values of the normalized sensitivity coefficient of area requirement with respect to the microalgal biomass yield using Eq. B.3 are shown in Figure B.1 and to the microalgal biomass maintenance using Eq. B.6 are shown in Figure B.2.

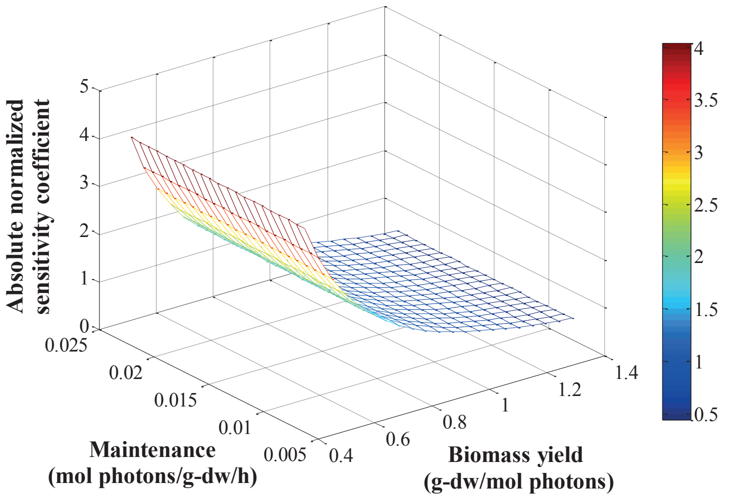

Figure B.1: Absolute normalized sensitivity coefficient of area requirement with respect to biomass yield on light energy based on annual light intensity and annual temperature of Peru, Huancayo

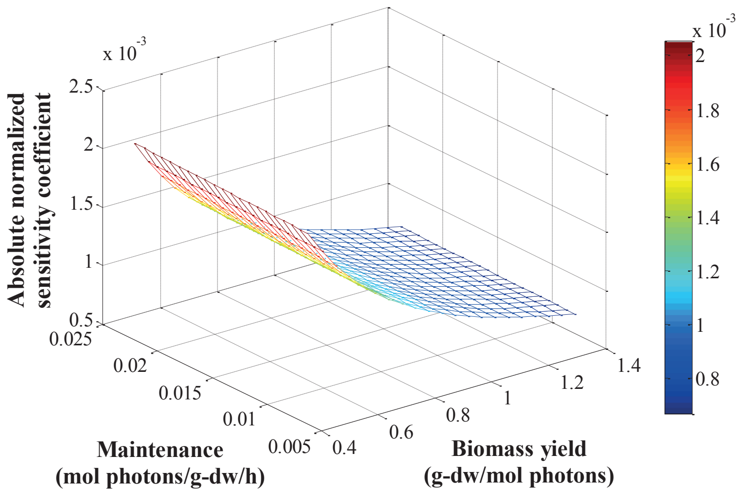

Figure B.2: Absolute normalized sensitivity coefficient of area requirement with respect to biomass maintenance based on annual light intensity and annual temperature of Peru, Huancayo

Summary

Recently, municipal wastewater has started to be considered as a potential resource of water, energy and nutrients nitrogen (N) and phosphorus (P). For example, the organic pollutants in municipal wastewater represent a potential chemical energy of 1.5–1.9 kWh per m^3 of wastewater. At present, conventional activated sludge (CAS) systems are widely applied to treat municipal wastewater. The main advantages of CAS systems are that they are robust and generally produce an effluent quality that meets the discharge guidelines. However, CAS systems cannot be considered sustainable, because these require large amounts of energy (mainly for aeration and sludge treatment), have a high CO_2 emission and do not recover valuable resources.

Chapter 1 describes new developments in municipal wastewater treatment and recovery technologies that can overcome the limitations of low temperatures and diluted valuable compounds from municipal wastewater. In this thesis new municipal wastewater treatment concepts that combine wastewater treatment with recovery of valuable resources and can save considerable amounts of energy were investigated by modelling and experiments.

Chapter 2 describes a procedure to design and integrate new process units into promising wastewater treatment plant configurations. A numerical Excel-based simulation tool was developed combining literature data and information from recent experimental research, and steady-state energy and mass balances with first-order conversions. Quantitative numerical results showed that a novel configuration with bioflocculation, cold partial nitritation/Anammox, novel P recovery, and anaerobic digestion is the most promising wastewater treatment concept for the Netherlands, because it can: 1) treat wastewater year round; 2) produce an effluent at a quality that meets the discharge guidelines; 3) reduce CO_2 emission by 35% compared to the CAS system; 4) achieve a net energy yield up to 0.24 kWh per m^3 of wastewater, whereas the CAS system have a negative net energy yield of -0.08 kWh per m^3 of wastewater; and 5) recover 80% of the sewage P. A sensitivity analysis of the proposed configuration points out the

dominant influence of wastewater organic matter on energy production and energy consumption. Additionally, it was also demonstrated that another configuration, which uses a similar approach with bioflocculation and anaerobic digestion but where N and P in the permeate of the bioflocculation are assimilated by microalgae, is not applicable in the Netherlands, because of a limited light availability, low temperature and low irradiance in the winter period.

In **Chapter 3** the feasibility of the two above-mentioned configurations that are based on combined bioflocculation and anaerobic digestion but with different nutrient removal technologies, i.e. partial nitritation/Anammox or microalgae treatment, was further evaluated for 16 locations around the globe with respect to their net energy yield, N and P recovery efficiencies, CO_2 emission and area requirements. The results quantitatively support the pre-assumption that the applicability of the two configurations are strongly location dependent. The configuration with (cold) partial nitritation/Anammox is applicable in tropical regions and some locations in temperate regions, such as Southern Europe and Southern part of South America. The configuration with microalgae treatment is only applicable the whole year round in tropical regions that are close to the equator line, such as Southeastern Asia and Northern part of South America. On the locations with very low sewage temperatures, e.g. temperatures below 10°C, for example in Northern America and Eastern Europe, CAS systems are recommended. A sensitivity analysis of the configuration employing microalgae treatment showed that microalgal biomass yield and nutrient concentrations in the municipal wastewater have a critical impact on the area requirement and effluent concentrations.

In CAS systems energy recovery from wastewater is accomplished by anaerobic digestion of the organic solids in primary and secondary sludge into methane. However, volatile fatty acids (VFA), which are intermediate digestion products, may be preferred over methane, because VFA can be used as starting compounds for a wide range of higher value products, for example bioplastics (polyhydroxyalkanoate or PHA) and medium-chain fatty acids. Production of VFA is only possible if the last step of anaerobic digestion, i.e. methanogenesis, can be prevented. This can be accomplished by applying a short sludge retention time (SRT) to actively wash-out the slow growing methanogens and/or by applying extreme pH values that inhibit growth of methanogens. In **Chapter 4** the feasibility of a combined process with bioflocculation, using a high-loaded membrane bioreactor (HL-MBR) to concentrate sewage organic matter, and anaerobic fermentation, using a sequencing batch reactor to produce VFA, was experimentally investigated. The results showed that an HL-MBR operated at a hydraulic retention time (HRT) of 1 hour and an SRT of 1 day resulted in very good performance, because as high as 75.5% of the sewage COD was diverted to the concentrate and only 7.5% was mineralized. It was also found that 90% of the sewage NH_4-N and PO_4-P were conserved in the HL-MBR permeate, which can be reused as irrigation water because it is free from solids and pathogens. During anaerobic fermentation of the HL-MBR concentrate at an SRT of 5 days and 35°C, a VFA yield of 282 mg VFA-COD/g VSS was reached and this was equivalent to only 15% of the sewage COD. Methane production was inhibited at an SRT of 5 days, but incomplete solids degradation mainly limited the VFA production.

Hence, the VFA yield from anaerobic fermentation needed to be increased. In **Chapter 5** it was hypothesized that high pH (pH 8–10) fermentation combined with a long SRT, allowing for sufficient solubilization of solids and colloidal COD, can improve the VFA yield. The results showed that application of a pH shock of 9 in the first 3.5 hours of a sequencing batch cycle followed by a pH uncontrolled phase for 7 days gave the highest VFA yield of 440 mg VFA-COD/g VSS and this was equivalent to 26% of the sewage COD. This yield was much higher than at fermentation without pH control or at a constant pH between 8 and 10. The high yield in the pH 9 shock fermentation could be explained by (1) a reduction of methanogenic activity, or (2) a high degree of solids degradation or (3) an enhanced protein hydrolysis and fermentation. This study also demonstrated that the VFA yield can still be further optimized by fine-tuning pH levels and longer operation, possibly with fermentative microorganisms adapted to a high pH that are commonly found in nature. This would further increase VFA yield to 33% of the sewage COD.

In **Chapter 6** three novel municipal wastewater treatment plant configurations based on combined bioflocculation in HL-MBR and high pH anaerobic fermentation but with different nutrient removal technologies, i.e. partial nitritation/Anammox or microalgae treatment, or without nutrient removal are further discussed. In the last configuration mentioned, HL-MBR permeate could be directly used as irrigation water but the amounts of micropollutants should be measured. In fact, because of the shorter SRT of the HL-MBR compared to CAS systems the removal efficiency of micropollutants may be lower and advanced post-treatment may be required. In the second configuration, the permeate of HL-MBR is treated by (cold) partial nitritation/Anammox to remove N and by a novel P recovery technology. In the current study it was assumed that cold partial nitritation/Anammox can be applied if the temperature of wastewater is above 10°C. However, this concept still needs further optimization. In particular the partial nitritation process at temperatures down to 10°C is challenging and oxygen control becomes crucial to avoid nitrate production. Moreover, the main challenge for P recovery is development of a cost-effective technology that can work at low wastewater temperatures and low phosphorus concentrations. In the third configuration, N and P in the HL-MBR permeate are assimilated by microalgae. The applicability of microalgae is determined by the production location. Because the area requirements for microalgae cultivation are still much higher than for CAS systems, a microalgae treatment would only be economically feasible if the applications of microalgal biomass will be able to produce a very high value product, such as carotenoids and dietary supplement. However, in this case only the nutrients should be allowed to come into contact with the microalgae.

In our experiments, the bioflocculated sewage organic matter had a concentration of 10 g COD/L, from which about 3.5 g VFA-COD/L could be produced. In order to make VFA recovery processes more attractive, the VFA production from a 20 g COD/L of bioflocculated concentrate becomes a promising candidate. This also indicates that in an HL-MBR the HRT needs to be decreased from 1 to 0.5 hours. However, the feasibility of an HL-MBR with such a low HRT needs to be further investigated with respect to membrane fouling, oxygen limitation and the extent of membrane area. Our experiments also show that at constant pH 9–10 a considerable amount of (soluble) proteins were not converted into VFA. To continue work in line with this thesis, further research should be conducted on (1) a more detailed chemical characterization of the remaining effluent produced from high pH fermenter of the HL-MBR concentrate, (2) the development of cost-effective VFA extraction technologies, (3) a life cycle assessment and financial analysis of a mixed VFA production and a single acid production, and (4) the distribution of heavy metals, pathogens and micropollutants in the HL-MBR and high pH fermenter as well as in the end products from these processes.

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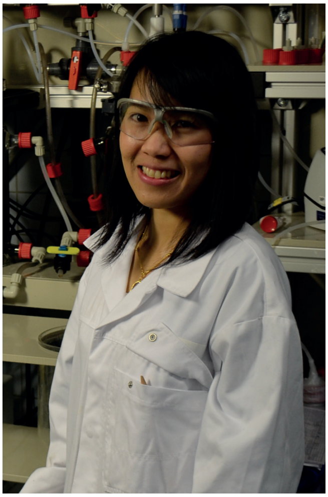
Rungnapha Khiewwijit
December 2015

About the author



Rungnapha Khiewwijit was born on February 5th, 1985 in Ratchaburi, Thailand. Her given nickname is Pom. After she completed high school at Satthasamut in Thailand, in 2004 she got a scholarship from the Royal Thai Government to do her bachelor's degree in Environmental Science at Van Hall Larenstein in Leeuwarden, the Netherlands. In 2009 she got a scholarship from Rajamangala University of Technology Lanna in Thailand to do her master's degree in Water Technology at Wetsus Academy, Leeuwarden. She obtained her Master of Science degree in 2011 by completing a thesis entitled 'Biological sulfide treatment in a 2-step process and inhibition of biological sulfide oxidation by benzene, toluene, dimethyl disulfide and methanethiol' at Wetsus, European centre of excellence for sustainable water technology in the Netherlands.

In September 2011, she started research on new municipal wastewater treatment concepts towards energy saving and resource recovery as a PhD student at the Biobased Chemistry and Technology department and the Sub-department of Environmental Technology in Wageningen University, but her research was performed at Wetsus in Leeuwarden.

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- SENSE Writing Week (2012)
- Environmental Research in Context (2012)
- Research in Context Activity: 'Co-organising Wetsus Water Challenge', Leeuwarden (2012)

Other PhD and Advanced MSc Courses

- Matlab Introduction Course, Wageningen University (2011)
- Working Safely in Laboratories, Wetsus (2011)
- Systems and Control Theory, Wageningen University (2012)
- Project and Time Management, Wageningen University (2012)
- Techniques for Writing and Presenting a Scientific Paper, Wageningen University (2012)
- Presentation Skills, Wetsus (2013)
- Matlab Course, Wageningen University and Wetsus (2013)
- Advanced English in Writing and Presentation Skills, DC Taleninstituut (2014)
- IMETE Summer School on Resource Recovery from Wastewater, Ghent University (2014)
- Biological Water Treatment and Recovery Technology, Wageningen University and Wetsus (2014)

Management and Didactic Skills Training

- Co-organising Environmental Technology department trip, Canada (2012)
- Supervising three MSc thesis students (2012-2015)
- Supervising three internship students (2012-2015)
- Co-organising Organic and Nutrients team meetings (2014)
- Co-organising Biobased Chemistry and Technology department trip, China (2015)

Oral Presentations

- *Energy and nutrient recovery from municipal wastewater: A scenario analysis for the Netherlands*. The 32nd Benelux Meeting on Systems and Control, 26-28 March 2013, Houffalize, Belgium
- *Resource recovery from municipal wastewater: Innovative design for the Netherlands and worldwide.* NL4Talents workshop - Holland alumni and career forum for international students, 23 November 2013, The Hague, The Netherlands
- *Deriving rules of thumb for the control of a novel wastewater treatment plant*. The 33rd Benelux Meeting on Systems and Control, 25-27 March 2014, Heijden, The Netherlands

SENSE Coordinator PhD Education

Dr. ing. Monique Gulickx

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